THE INFLUENCE OF
SOIL ORGANIC MATTER ON SOIL STRUCTURE

by

KEITH CHANEY

A Thesis Presented to

the University of Edinburgh

for the

Degree of Doctor of Philosophy

in the Faculty of Science

September, 1978

DECLARATION

I declare that I have composed this thesis myself. The work embodied in it is the result of my own investigations except where reference has been made to published literature.

CONTENTS

SUMMARY

Several methods were assessed for measuring the stability of soil aggregates; these were wet-sieving, leaching with sodium choride, slaking tests, water-drop method and a modified moisture characteristic method. The wet-sieving method was selected for use in further experiments because (a) it gave reproducible results, (b) it distinguished between all the soils tested, and (c) the results were consistent with the behaviour of the soils in the field.

A survey of over one hundred predominantly heavier textured soils from the East of Scotland and England showed that there was a highly significant correlation between total organic matter content and aggregate stability. Two soil organic matter components, namely polysaccharide and humic acid, were also found to have highly significant correlations with aggregate stability. These results indicate that both polysaccharide and humic acid are involved in the stabilisation of soil aggregates, but do not show that one of the organic matter fractions is more important than the other.

The sodium hydroxide extractable humic acid was generally better correlated with aggregate stability than the pyrophosphate extractable humic acid. This suggests that the less oxidised, higher molecular weight humic acid is more important in the stabilisation of soil aggregates than the more oxidised, lower molecular weight humic acid of the pyrophosphate extract.

Incubations carried out in the laboratory have shown that a physical addition of 0.5% glucose, to finely ground soil, is capable of promoting the reformation of stable aggregates. Experiments have shown that the glucose is respired largely in two to three weeks. Therefore, the stabilising agency must be extracellular poly-

saccharide produced from the glucose by microorganisms. Stable aggregates were also reformed when physical additions of polysaccharide material, humic acid and fulvic acid were made to finely ground soil. In these incubations it is thought that aggregates could be reformed due to:-

(a) extracellular polysaccharide being produced by microorganisms from metabolisable material, (b) the gluing action of the large molecular weight polymers, and (c) the subsequent adsorption of the large molecular weight polymers. In all incubations in which physical additions of organic material were made, the stability of the reformed aggregates was transient and declined after two to four weeks.

Adsorption of humic acid onto the soil with subsequent incubation also reformed stable soil aggregates. The stability of the reformed aggregates was greater when glucose was added at the beginning of the incubation period. In both cases, the stability of the reformed aggregates was maintained and showed no signs of decreasing over a period of eight weeks. The extracellular polysaccharide produced by the microorganisms is initially effective in reforming stable soil aggregates. It would then appear that humic substances are capable of the long-term stabilisation of these aggregates, after a period of incubation.

ACKNOWLEDGEMENTS

I acknowledge with deep gratitude the advice and guidance given by Dr R.S. Swift throughout the course of this study, which he supervised.

Thanks are due to the technical staff of the Soil Science Department for the help given with analytical work and to Mrs P. Allan and Miss S. Stevenson for typing this thesis.

Finally I would like to thank the Agricultural Research Council who provided the financial support that made this investigation possible.

K.C.

1. INTRODUCTION

The fact that soils under grass generally possess a better structure than similar soils which have been cultivated has been general knowledge in the farming community for hundreds of years. The local influence of factors such as climate, topography and soil properties combined together with the effect of grassland on soil structure have led to distinctive rotational systems in different areas of Great Britain e.g. the Norfolk four-course rotation. These systems were designed to keep the land in "good heart", that is fertile, free from weeds and in good structural condition, but at the same time give maximum economic returns.

Many investigations have been carried out since the middle of the nineteenth century comparing the yields of various crops grown continuously and in rotations. For instance, the Classical Rothamstead Experiments (Rothamstead Experimental Station, 1970) were set up to look at the effect of natural and artificial manures on the continuous growth of different crops. Russell and Voekler (1936) suggested that the deterioration of yields encountered at Rothamstead and in similar experiments at Woburn was probably associated with the exhaustion of organic matter in the soil. However, it was not until the introduction of heavy machinery and intensive farming systems that concern was shown for the adverse effect that this method of farming might be having on soil structure, due in part to the declining organic matter levels.

The problems associated with intensive cultivation were highlighted recently in a report made by the Agricultural Advisory Council (1970). This made the following points:- "Some soils are

suffering from dangerously low levels of organic matter and cannot be expected to sustain the farming systems which have been imposed on them"; (Paragraph 12).

"Organic matter declines with a reduction of grass in rotations, and will tend to stabilise at a new lower level according to the cropping system; whether or not this level is satisfactory to retain good soil structure will depend on soil type, cropping practice and cultivation requirements. On inherently unstable soils the ploughing up of grassland and adoption of an all-arable rotation with its lower organic matter level can create serious structural problems". (Paragraph 212).

A survey carried out in the East of Scotland (Spiers, 1976) produced figures for the organic matter content of soils which support the findings of the Agricultural Advisory Council. The mean organic matter content increased as grass was introduced into an arable rotation for soils in a given textural class.

Soil organic matter itself is a complex material, consisting of a whole series of products which range from fresh plant, animal and microbial residues, through ephemeral products of microbial decomposition to fairly stable amorphous, brown to black decomposed material. Chemically, soil organic matter is made up of components such as humic substances (e.g. humic and fulvic acids), polysaccharides, proteins, fats, waxes, tannins, simple organic compounds etc.

The fresh and decaying plant and animal material together with organic deposits (e.g. coal) are not of direct importance in studies of soil structure. It is the 'active' organic material in close association with the soil mineral particles (e.g. polysaccharides and humic substances) which probably contribute to the formation and

stabilisation of soil aggregates (Greenland, 1965 a and b).

As one of the 'active' organic components soil polysaccharides have been closely studied in relation to the aggregation of soil particles. In fact over the last fifty years a great deal of evidence has been collected showing that they can be involved in aggregation (Martin, 1946; Aspiras et al, 1971; Martin, 1971; Martin et al, 1972; Bab'yeva and Moavad, 1973). The predominant conclusion put forward is that soil polysaccharides are responsible for the initial stages of aggregation, i.e. those processes involved in aggregate formation. The binding properties of soil polysaccharides enable them to form soil aggregates, but because they are degraded by microorganisms the polysaccharide cannot be responsible for long-term aggregate stabilisation. At the present date no soil organic matter constituent has been shown to be capable of long-term stabilisation of the aggregates formed by the action of polysaccharides.

If there were such a constituent it would have to be resistant to microbial attack and be capable of some type of binding action to hold individual mineral particles together to form a soil aggregate. Humic substances are a major group of compounds within soil organic matter which have not been studied in great depth in relation to soil aggregation, yet have the properties mentioned above.

Much remains to be studied concerning the influence of soil organic matter as a whole, and of its individual components in relation to aggregate formation and stabilisation. A major proportion of this thesis will be concerned with looking at the relationship between the amount and composition of soil organic matter and the aggregate stability of soils collected from various parts of England and Scotland. Soils have been sampled at a wide

selection of sites from a number of soil series under different rotational systems to give a range of soil organic matter contents. Where possible pairs of soils of the same series have been taken from adjacent fields under permanent pasture and continuous cultivation.

In addition, through laboratory studies it is proposed to examine the role of soil organic matter constituents, especially humic substances, and polysaccharides in forming and then stabilising soil aggregates. Experiments will be carried out to assess the effect of the interaction of these materials with the mineral particles of the soil.

LITERATURE REVIEW

2. LITERATURE REVIEW

The literature review deals with the nature, properties and interactions of organic matter and clays; two of the soil constituents largely responsible for soil aggregation. This is followed by a consideration of soil aggregation and the factors influencing aggregate formation, degredation and stabilisation. Finally, the methods used for assessing aggregate stability are reviewed.

Since this review covers such a wide field of work only subjects which are of direct relevance to this study are examined in depth. Whereas other aspects, no less important in themselves but of peripheral interest, are dealt with less fully.

2.1. SOIL ORGANIC MATTER

2.1.1. The Origins and Forms of Soil Organic Matter

The main input of organic material into the soil is through the addition of plant and animal debris. Another source is the indigenous microbial population, which contributes through the excretion of organic compounds and the tissue of microorganisms upon death. In some situations this contribution by microorganisms can account for a significant amount of the total organic material added to the soil.

Organic debris which has recently been added to the soil still retains many characteristics of the original material, and is termed fresh organic matter. As this tissue is decomposed by microorganisms many changes occur and a large number of products are formed, some of which are persistent and some transient. In fact soil organic matter consists of a whole series of products, which range from recognisable undecayed plant and animal tissues through

ephemeral compounds of decomposition to highly decomposed products. This process is known as humification, the final product being the stable, amorphous, brown to black material normally referred to as soil humus.

Humus is a complex material which bears no resemblance to the original plant animal or microbial tissue and does not exhibit a constant chemical composition and structure. The actual composition will depend on a number of factors including original plant material, soil type, microbial population and climate. The most important elements in its structure are hydrogen, carbon and oxygen, with significant amounts of nitrogen, phosphorus and sulphur, but it also contains small amounts of most elements found in plant tissue (Kononova, 1961).

Physically, organic matter can be divided into free and adsorbed forms. Free denotes single isolated particles or organic matter that might consist of undecomposed plant remains, the less degradable, lignified plant tissues which are relatively low in humic substances or discrete particles of well-humified material.

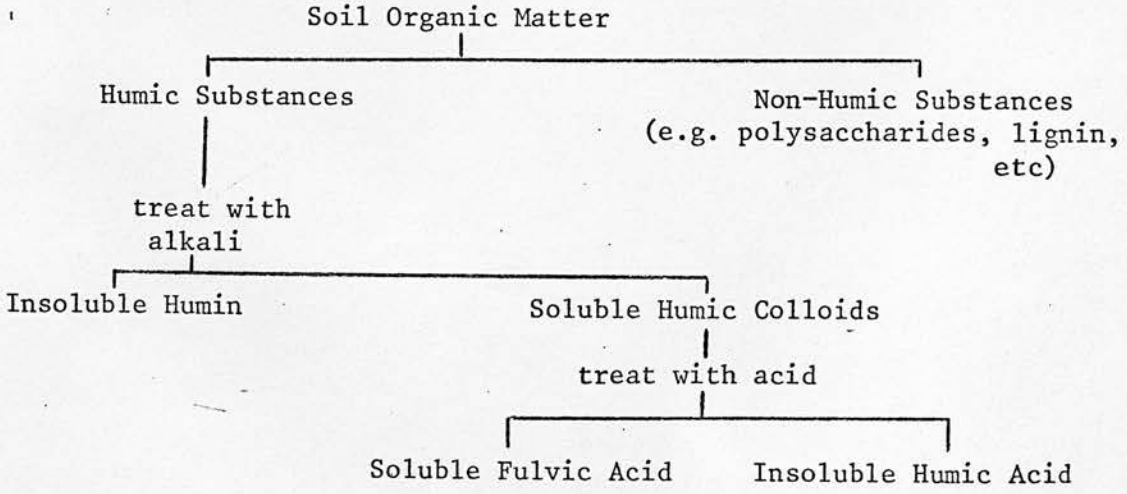
On the other hand some soil organic matter has been shown by many workers (Greenland and Ford, 1964; Schnitzer and Skinner, 1964) to be adsorbed by clay and other mineral particles. In most soils a large proportion of the organic matter interacts with the inorganic colloids to form the clay-organic complex, and this has a profound influence on the physical, chemical and biological properties of the soil (Greenland, 1965 b). Although some understanding of the interaction between clays and defined organic compounds (Greenland, 1965 a) has been obtained, an appreciation of the mechanisms involved in the formation of a natural clay-organic complex is hindered by an

inadequate knowledge of the detailed structure and composition of soil organic compounds. Since the formation of organo-clay complexes could have a significant effect on the formation and stabilisation of soil aggregates in arable and grassland situations, it is necessary to have some understanding of the nature and composition of the organic constituents.

2.1.2. The Composition of Organic Matter Constituents

Soil organic matter can be divided into humic and non-humic substances (Figure 1). The non-humic substances (such as polysaccharides, proteins, fats, waxes, tannins and simple organic compounds) are those which can be characterised and identified as belonging to a known group of compounds. The term humic substances is used to denote that group of closely related organic compounds which are dark brown in colour, amorphous, high molecular weight, exhibit colloidal properties and, in contrast to the non-humic substances, cannot be readily characterised chemically. Humic substances can be further subdivided into three fractions, namely humic acids, fulvic acids and humin, on the basis of solubility in acid and alkali.

Figure 1. Fractionation of Soil Organic Matter



2.1.3. Non-Humic Substances

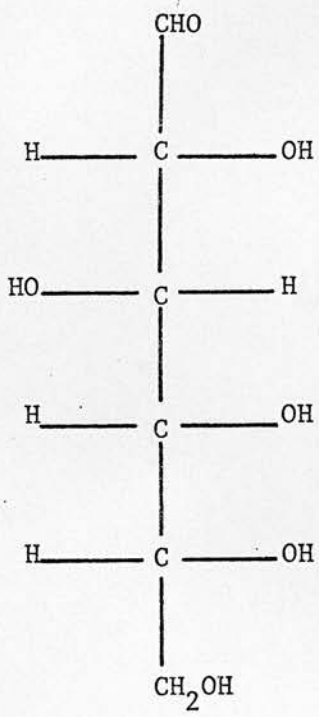
2.1.3.1. Carbohydrates

The term carbohydrate is used to denote compounds that are hydrates of carbon, the simplest possessing the general formula $C_n H_{2n} O_n$ (Percival, 1955). It was established at the beginning of this century by carrying out methylation and oxidation experiments (e.g. Haworth, 1928) with evidence from X-ray spectroscopy that glucose existed in ring form. However, for monosaccharides in solution there is an equilibrium between the cyclic and acyclic forms, although the proportion of acyclic aldehydic and ketonic forms is very small indeed. These forms and the actual conformation are given in Figure 2 for glucose.

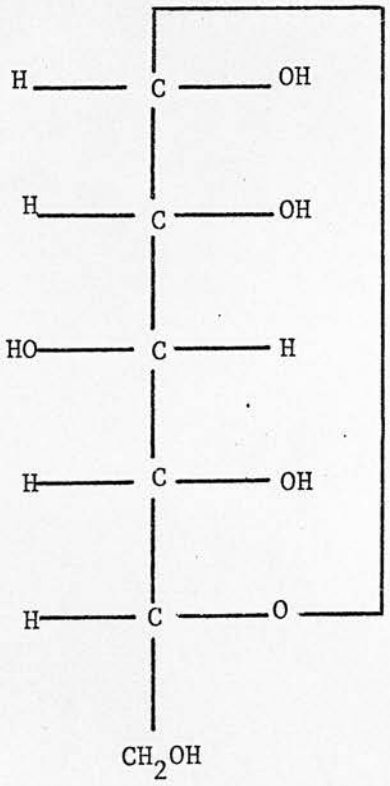
More complex compounds such as dissaccharides and polysaccharides are formed by the combination of simple sugars together with the elimination of water molecules. The reverse of this reaction is the hydrolysis of complex carbohydrates into monosaccharide units by dilute acids or enzymes (Mahler and Cordes, 1966). Unlike monosaccharides which are reducing, soluble in water and sweet to the taste, the polysaccharides are frequently insoluble, all are non-reducing or nearly so and tasteless.

A variety of different types of linkages are found in polysaccharides. Starch is a polymer of D-glucose molecules linked by α-(1→4) glycosidic bonds (Figure 3a). It is an α linkage if the OH groups of the glucose molecules joined together are both below the plane of the ring, and (1→4) refers to the ring number of the carbon atom of each glucose molecule involved in the bond. Cellulose is also a polymer of D-glucose but it is linked by β-(1→4) glycosidic bonds (Figure 3b). In this case one OH group is above the plane of

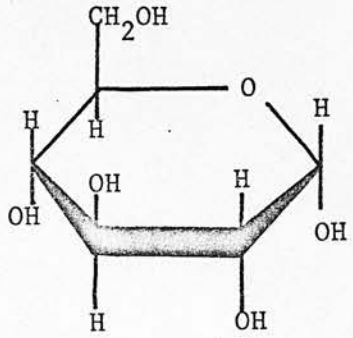
Figure 2 Representations of the ∝-D-Glucose Molecule



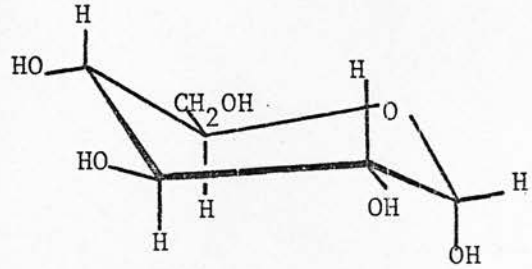
D-glucose



∝-D-glucose



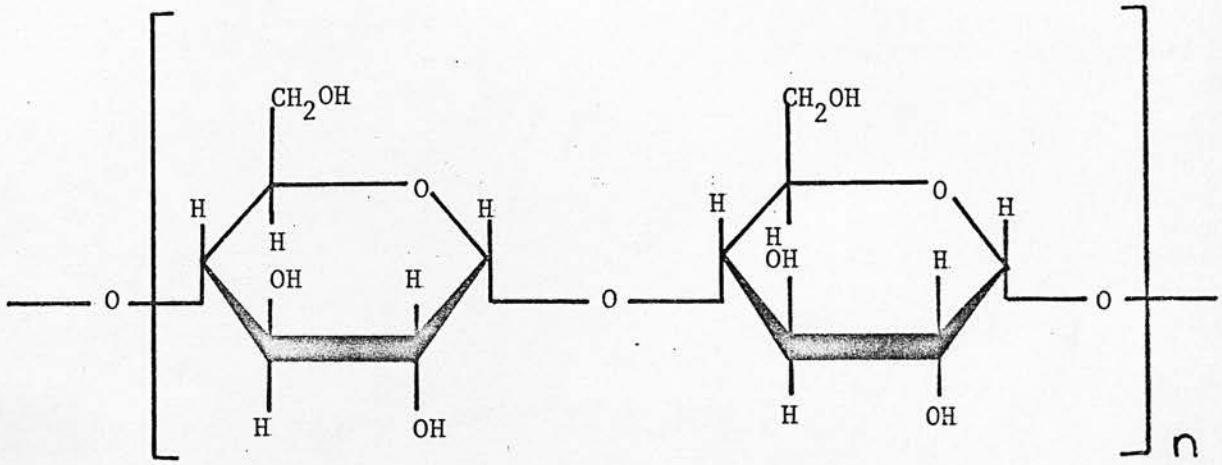
glucopyranose ring
∝-D-glucose



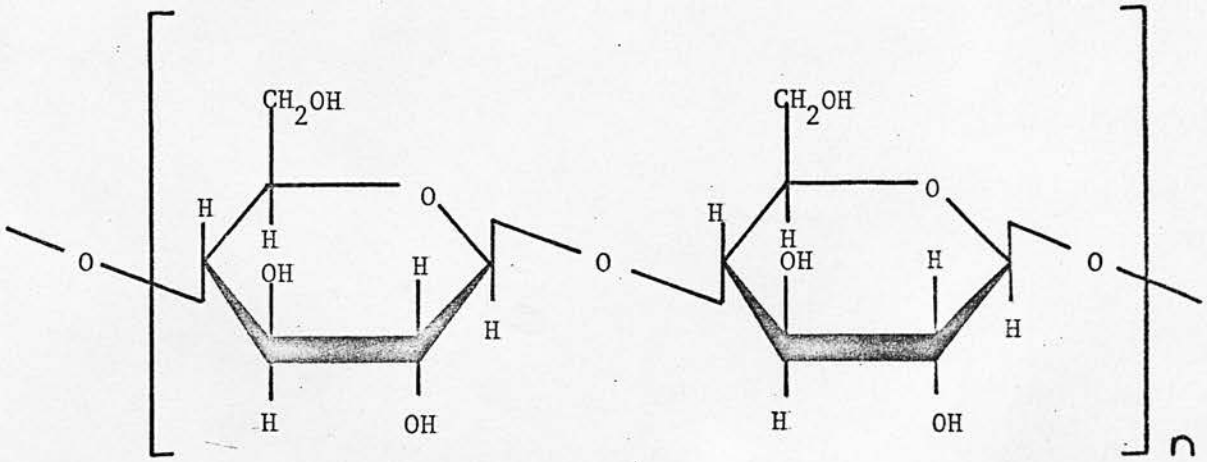
conformation of the
chair form
∝-D-glucose

Figure 3 The Glycosidic Bonds of Starch and Cellulose

(a) Starch α-(1→4)-glycosidic bonds



(b) Cellulose β-(1→4)-glycosidic bonds



the glucose ring and the linkage is termed β. β-(1→3) and β-(1→6) linkages are two other common linkages of polysaccharides.

The origin of natural carbohydrates is the process of photosynthesis. This involves the utilisation of the energy from sunlight to convert carbon dioxide and water to simple sugars. As a result of natural food chains carbohydrates are found universally distributed among plants, animals and microorganisms. The most abundant carbohydrates are often polysaccharide in nature and usually have one of two functions, namely skeletal or food storage. Examples of skeletal polysaccharides are cellulose and chitin, glycogen and starch are two storage polysaccharides.

Whereas plant polysaccharides tend to be polymers of a single sugar (e.g. cellulose formed from glucose), the polysaccharides that exist in the soil usually have several different monomer sugars giving rise to complex compositions. Cheshire (1977), when providing data for the content of sugars in the hydrolysate of a typical arable Scottish soil (5.6% C), listed glucose, galactose, mannose, xylose, arabinose, fucose, rhamnose, galacturonic acid, glucuronic acid, galactosamine and glucosamine as the digest monosaccharides. The same monosaccharides have been identified by several workers (Hayes and Swift, 1978). Work using ^{14}C-labelled substrates (Oades, 1974) to study either polysaccharide synthesis by the soil microorganisms or the rate of decomposition of plant material, indicates that hexose and deoxyhexose sugars are of microbial origin and pentose sugars are derived from plant material (Cheshire, 1977).

2.1.3.2. Other non-humic substances

This is an extremely diverse group of substances which includes the constituents of decomposing plant residues, various

products of microbial activity and products of re-synthesis in the form of bacterial synthesis. Substances considered in this section include amino acids, proteins, fats, waxes, resins, lignins and tannins.

Proteins are essential components of all living systems from the most elementary to the most complex. They serve as enzymes, antibodies, structural elements, transport devices and metabolic regulators, and are therefore involved in all physiological processes. Proteins are polymeric macromolecules; the monomers being a group of about twenty amino acids. These amino acids are linked, by peptide bonds, in different combinations to form proteins with molecular weights of up to several million. However, these proteins do not exist as separate entities in the soil, because of their susceptibility to microbial attack. It has been shown by several workers (e.g. Estermann et al, 1959) that proteins are adsorbed by clay minerals and this process can protect the protein from micro-organisms. Amino acids or peptide residues can also be protected from microorganisms by incorporation into humic substances.

Many of the remaining non-humic substances listed above, which have been isolated in soil extracts, were constituents of plant cells (Clowes and Juniper, 1968). Cutin and suberin are both cross-linked polymers comprised of long-chain hydroxy fatty acids. Both these compounds are relatively resistant to chemical or enzymatic attack, having a protective role in the plant. Waxes are a heterogeneous assembly of compounds associated with suberin and cutin in the plant cell wall. They consist of mixtures of esters of higher aliphatic acids and higher aliphatic or acyclic alcohols, long-chain paraffins, ketones and acids.

Lignin is one of the most abundant plant polymers which acts as a waterproof cement in the cell wall of plants. It is a polymer of various derivatives of phenyl propane, namely p-coumaryl, coniferyl and sinapyl alcohols (Brown, 1964).

Although tannins are a heterogeneous collection of polyhydroxyphenolic compounds they may be divided into two main groups. First, there are hydrolysable tannins, which yield carbohydrates and phenolic acids on hydrolysis. Secondly, there are condensed or non-hydrolysable tannins which contain little or no carbohydrate, and are made up of flavan-3-ol or flavan-3, 4-ol.

Tannins, fats, waxes, lignin, etc. (unlike proteins and carbohydrates) can exist in the soil without being protected by clay minerals. This is because these compounds are relatively resistant to microbial attack, and can therefore persist in the soil for long periods after plant remains are deposited.

2.1.4. Humic Substances

2.1.4.1. Chemical properties

The chemical composition of humic substances is variable, the carbon content usually lies between 45% to 60%, the oxygen content between 30% and 48%, the hydrogen content between 3% and 6%, the nitrogen content between 0 and 6% and other components in small amounts. It has been found (Dubach and Mehta, 1963) that the carbon content increased and the oxygen content decreased with increasing molecular weight. The nitrogen content of humic substances increases with molecular weight. Swift and Posner (1972) found that the increase in total nitrogen was due mainly to an increase in the amino acid nitrogen, but a substantial proportion was not identified.

Most of the oxygen present in humic substances is in the form of functional groups, namely carboxyl (-COOH), phenolic (Ar-OH) and alcoholic ($-CH_2OH$) hydroxyls and carbonyl [in aldo ($-\overset{H}{\underset{|}{C}} = O$), keto ($-C = O$) or enol ($-C = \overset{OH}{\underset{|}{C}}$) forms] groups. Other oxygen containing functional groups present in significant amounts are quinone, methoxyl, ether and ester groups.

There are many non-oxygen-containing functional groups present in humic substances, such as the amine ($-NH_2$) and thiol (-SH) groups. Whereas some of the oxygen containing functional groups lose their hydrogen ion to become negatively charged (e.g. carboxylic and phenolic) the amine group can gain a hydrogen ion to become positively charged:-

$$-COOH \rightleftharpoons -COO^- + H^+ \quad (a)$$

$$-NH_2 + H^+ \rightleftharpoons -NH_3^+ \quad (b)$$

At normal soil pH, reaction (a) is more likely to occur than (b).

The presence of considerable amounts of acidic and other functional groups gives rise to many charged sites on the humic polymer. The participation of these functional groups in cation-exchange reactions gives rise to one of the most important properties of humic substances, i.e. the capacity to retain and exchange cations. This plays an important role in the supplying of nutrients to plants and for the general maintenance of soil fertility.

The electric charge on the soil colloids is balanced by an equivalent amount of oppositely charged ions, the so-called exchangeable or gegen ions, held to the surface by mainly Coulombic forces. In addition to Coulombic forces there are also specific forces (Van der Waals-London forces) increasing the strength of bonding of certain ions. In soils the most common exchangeable cations are Ca^{2+}, Mg^{2+}, H^+, K^+, Na^+ and NH_4^+, calcium generally

being the dominant ion, with the relative abundance of the other ions varying greatly. The cation-exchange capacity of humic substances is very high (in the order of 300-400 meq/100g at neutral pH) compared with that of mineral components (Table 1), and although they are generally less abundant than the inorganic colloids they often make a major contribution to the overall cation-exchange capacity of the soil.

As with all charged colloidal systems the counterions are not held tightly at the surface of the colloid, but because of thermal motion and other factors they form a diffuse layer or ion swarm around the colloidal particle. The structure of this layer and its extension from the colloidal surface are determined by the surface charge density, kind of counterions, temperature and concentration of electrolytes in solution. The exchangeable ions are surrounded by water molecules and may thus be considered as forming a solution, which is often called the micellar solution in distinction to the outer solution of free electrolytes, the so-called intermicellar solution.

Humic substances are also highly efficient at combining strongly with a large number of heavy metal cations, some of which are essential plant micronutrients. For example, manganese, iron, cobalt, nickel and copper are all transition elements, which can be complexed by humic substances. The property of these metals which allows the formation of ligand-metal complexes is that they usually possess an incomplete set of electrons in the *d* level. The lone pairs of electrons of oxygen or nitrogen atoms in functional groups of humic substances, are then shared with the transition elements. It was stated earlier that there is a large number of functional groups containing oxygen and nitrogen, there-

fore the ligand-metal complex can be a very important process through which cations are held in the soil, in addition to simple ion-exchange.

Several workers have suggested that humic substances can form chelates (a more specific form of complex) with suitable metallic cations (e.g. manganese and copper). Himes and Barber (1957) showed that methylation of hydroxyls reduced chelation, which is circumstantial evidence for these functional groups being involved, as well as carboxyl and other groups.

Degradation of humic substances Several types of degradation reactions have been used to try and obtain information about the structure of humic substances (Hayes and Swift, 1978). In each reaction the polymer is broken down and the products analysed for the presence of specific compounds, using techniques such as infrared spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. These procedures are relatively simple where the monomer units are linked by labile bonds, such as the peptide bond in proteins, or glycosidic linkages in polysaccharides, since these are susceptible to hydrolysis in acid or alkaline conditions. However, in humic substances the monomer components are linked by much stronger bonds, such as C-C sigma bonds, and ether linkages, which are cleaved only by high energy processes. These processes must be closely controlled to avoid degradation of the polymer to very simple but structurally meaningless products.

Oxidation, reduction, hydrolysis, nitration, alkali at high temperature and alkali fusion are some of the degradative reactions carried out on humic substances (Dubach and Mehta, 1963). These reactions have shown that, unlike carbohydrates and proteins, humic substances do not have a common monomer but are mainly comprised of linked, substituted aromatic and phenolic units. For example,

oxidation with aqueous potassium permanganate has yielded aliphatic carboxylase acids, benzenecarboxylic acids and phenolic acids, (e.g. Matsuda and Schnitzer, 1972). Other products from this process have indicated the presence of aliphatic side chains (unsaturated and saturated) and lignin type structures in humic substances.

Recent work in this field has involved attempting to chemically, enzymatically or biologically synthesise humic type substances from known starting materials, and compare their compositions and physical and chemical properties with those of natural humic polymers (Haider and Martin, 1967; Haider et al, 1977).

2.1.4.2. Physical properties

Molecular weight. One of the fundamental physical properties of any chemical compound is its molecular weight. For a simple organic compound this is a single definable value which can be accurately determined, but with polymeric materials the situation is more complex. Humic substances are naturally occurring polymers that have relatively wide spreads of molecular weight; polymers exhibiting such spreads are termed polydisperse.

Before 1960 there was a large discrepancy between the results of molecular size measurements, for example, those obtained by electron microscopy (Flaig and Beutelspacher, 1951; Weisemuller, 1965) and molecular weight determinations (Weisemuller, 1965).

It was not until 1963 that Mehta et al, suggested that the differences between the two methods existed because the humic substances represent polydisperse systems and there were low molecular weight impurities contaminating the samples. Indeed, the technique of fractionation by gel chromatography showed that humic substances had a range of molecular weights varying from one thousand to several hundred thousands.

Cameron et al (1972) decided that whole humic substance extracts are usually too polydisperse to make reliable molecular weight measurements in the ultracentrifuge by the sedimentation velocity technique. Consequently, they fractionated with respect to molecular weight into fractions of low polydispersity and obtained values that ranged from 2×10^3 to 1.5×10^6, the higher figure not necessarily being the upper limit.

Molecular shape and size Several of the methods used for determining the molecular weight of polymers can also be used to determine their shape and size, particularly if they involve considerations of frictional forces acting on solute macromolecules as they move through solvent media. The magnitude of these frictional forces is related to the shape and sizes of the macromolecules.

Flaig and Beutelspacher (1968) concluded that humic acid particles are approximately globular from ultracentrifugation, viscosity and electron microscope studies. However, when these experiments were performed in the presence of sodium chloride, it appeared that the shape deviated from globular, to ellipsoidal shapes. Cameron et al (1972) concluded that the humic acid molecule in solution has the conformation of a randomly coiled polymer, in which branching may be significant, particularly at high molecular weights. These proposals were made on the basis of frictional parameter calculations.

The random coil model infers an open molecular structure that permits the perfusion of solvent molecules into and through the polymer. Such a structure is more consistent with our knowledge of the chemical nature, mode of formation and behaviour of humic substances than the globular model which implies a condensed, solid

molecular configuration. Strong evidence in favour of this theory is the gel-like behaviour of humic acids with water; they have been shown to take up many times there own weight of water.

In their study, Cameron et al (1972) obtained values for the spherical radii of the molecules which range from 1.5 nm for a molecular weight of 2,500 to 25.5 nm for a molecular weight of 1.4×10^6. These values agree well with some of those reported by Flaig and Beutelspacher (1968).

2.2. SOIL CLAYS

The topic of soil clays is very diverse, and a full discussion is beyond the scope of this study. For a comprehensive account of this subject the reader should consult Grim (1968). In this section only those properties of clays which are important in clay-organic interactions will be considered.

2.2.1. The Structure of Clay Minerals

Clay minerals are layered alumino/silicates and the basic structural units forming the crystal lattice are two ionic co-ordination groups, namely the silicon/oxygen tetrahedron and the aluminium/oxygen octahedron. An interlocking plane of a series of silicon tetrahedra held together by sharing oxygen ions, gives a sheetlike tetrahedral layer. Similarly large numbers of aluminium octahedra, bound together by shared oxygens or hydroxyl groups, are arranged in a plane to produce an octahedral layer. When aluminium is present in the octahedral layer, only two-thirds of the possible co-ordination positions are filled to balance the structure; this is a gibbsite-type structure. When magnesium is present, all the possible positions are filled to balance the structure; this is a

brucite-type structure.

The tetrahedral and octahedral layers are held together by the apical oxygen of the tetrahedral sheet replacing one oxygen or hydroxyl position of the octahedral sheet. Different combinations of these two general structural layers, the tetrahedral and octahedral sheets, yield the structures of the various layer silicates of importance in soils, e.g. smectites, hydrous micas, kaolinites etc.

On the basis of the number and arrangement of tetrahedral (silica) and octahedral (alumina) layers contained in the crystal units, silicate clays can be classified into four main groups:-

1:1 type minerals (1 silicon : 1 aluminium) e.g. kaolinite.

2:1 type minerals (1 silicon : 1 aluminium : 1 silicon) which expand between crystal units e.g. montmorillonite

2:1 type non-expanding minerals e.g. illite.

2:2 type minerals (1 silicon : 1 aluminium : 1 silicon : 1 aluminium) which do not expand e.g. chlorite.

There are many clay minerals in each of these four groups, each member of a group usually having a different chemical composition. These differences are due to isomorphous substitution of the aluminium in the octahedral layer and/or of the silicon in the tetrahedral layer. For example, nontronite and saponite are both members of the smectite group of clay minerals. In smectites there can be isomorphous substitution in the tetrahedral layer (Al^{3+} for Si^{4+}) or the octahedral layer. The main difference between nontronite and saponite is due to the isomorphous substitution in the octahedral sheet. Replacement of aluminium by iron (Fe^{3+}) yields nontronite; this is a dioctahedral mineral because only 2

out of every 3 possible spaces are filled. Whereas in saponite, a trioctahedral mineral, there is total replacement of 2 Al^{3+} by 3 Mg^{2+}. Although there are several different substitutions to give rise to different members, all the minerals in the smectite group have the same charge per unit cell (0.66).

2.2.2. Source of the Negative Charge of Clay Minerals

The causes of cation-exchange capacity of the clay minerals can be considered under three headings.

Exposed crystal edges. Broken bonds around the edges of the silica-alumina units would give rise to unsatisfied charges, which would be balanced by adsorbed cations. The broken bonds would tend to be on non-cleavage surfaces and hence on the vertical planes, parallel to the C axis, of the layer clay minerals. In kaolinite and halloysite minerals this is probably the major cause of exchange capacity. In illite and chlorite minerals, broken bonds are an important cause of exchange capacity, and when these minerals are well-crystallised and have a relatively low exchange capacity, it may be the major cause. In smectite and vermiculites, broken bonds are responsible for a relatively small proportion ($\sim$20%) of the cation-exchange capacity.

It is thought that hydroxyls attached to the silicons of the broken tetrahedral units would be ionised in a similar way to ordinary silicic acid, that is :

$$Si - OH + H_2O \rightleftharpoons SiO^- + H_3O^+,$$

causing a negative charge on the lattice. The positive charges may originate from exposed octahedral groups which react as bases by accepting protons. The negative charge would grow and the positive charge decrease with rising pH, as a result of increasing ionisation of the acid groups and decreasing proton addition to the

basic groups. This phenomenon has given rise to the term "pH dependent charge" of inorganic colloids.

Ionic substitution. Substitutions within the lattice structure of trivalent ions for quadrivalent silicon in the tetrahedral sheet and ions of lower valence, particularly magnesium, for trivalent aluminium in the octahedral sheet, result in unbalanced charges in the structural units of some clay minerals. Sometimes such lattice substitutions are balanced by other lattice changes, for example hydroxyl for oxygen, but frequently they are balanced by adsorbed cations.

Exchangeable cations resulting from lattice substitutions are to be found mostly on cleavage surfaces, e.g. the basal cleavage surfaces of the layer silicate minerals. The charges resulting from substitutions in the octahedral sheet act through a greater distance than the charges resulting from substitutions in the tetrahedral sheet. Therefore, it would be expected that cations held because of lattice substitutions in the tetrahedral sheet would be bonded by a stronger force than those resulting from substitutions in the octahedral sheet. In some cases cations held by forces due to substitution of aluminium for silicon seem to be substantially non-exchangeable, e.g. potassium in micas. In clay minerals, replacements in the octahedral layer are probably the major substitutions causing cation-exchange capacity. In montmorillonite, substitutions within the lattice cause about 80% of the total cation-exchange capacity.

The hydrogen of exposed hydroxyls. The hydroxyl groups are, in this instance, an integral part of the structure rather than due to broken bonds. The exposed hydroxyl may have the hydrogen replaced

by a cation, which would be exchangeable. However, it seems possible that such hydrogen would be relatively tightly held and, in the main, not replaceable.

At this point it should be noted that the source of negative charge of clay minerals is different to that of organic colloids, in which the functional groups give rise to the cation-exchange capacity.

2.2.3. Cation-Exchange Capacity

In clay minerals in which the cation-exchange capacity results from broken bonds, the exchangeable cations would be around the edges of the flakes and elongate edges. In the clay minerals where the exchange capacity is due to lattice substitution, the cations are mostly on the basal plane surfaces.

When a clay has relatively small amounts of adsorbed water (say sufficient water to develop plasticity) then it is likely that the adsorbed cations around the edges of flakes are held directly in contact, or at least very close to the clay mineral surface. When the amount of water is at least that required for the plastic state, the exchangeable cations may be at greater distances from the clay mineral surfaces and separated from them by water molecules. In any given system the position of the exchangeable cations with respect to the clay minerals surface will not be the same.

The rate of cation-exchange varies with the clay mineral, the nature of the cations, and the nature and concentration of the anions. In general the reaction of kaolinite is most rapid, being almost instantaneous. Apparently exchange on the edge of the particles can take place quickly, but penetration between the

sheets takes more time. The time for illite to reach completion can be hours, perhaps days, due to part of the exchange occurring between basal flake surfaces firmly held together. Exchange in vermiculite is intermediate between these, because a certain time is required for penetration between the large flakes.

The cation-exchange capacity of clay minerals ranges from 3-150 meq/100g (Table 1).

Table 1. Cation-exchange capacity of clay minerals

Clay	CEC (meq/100g)
Kaolinite	3 - 15
Smectite	80 - 150
Illite	10 - 40
Vermiculite	100 - 150
Montmorillonite	80 - 100
Chlorite	10 - 40

2.2.4. The Nature of the Clay Surface

The broken edges of the crystal lattice give rise to unsatisfied oxygen and hydroxyl ions on the vertical surfaces of all the clay minerals. The negative charge of these groups is satisfied by a diffuse layer of cations.

The exposed horizontal surfaces of clay minerals present either a layer of oxygen atoms or hydroxyl groups, that are part of the mineral structure. Kaolinite has one horizontal surface composed of oxygens and the other composed of hydroxyls. Whereas, the two exposed basal surfaces of smectites are composed of hydroxyls, and those of illites are composed of oxygens. The horizontal surfaces are hydrated and are covered with a diffuse layer of cations, satis-

fying the negative charge caused by isomorphous substitution within the lattice.

The position of the cations and the effect of water were dealt with in section 2.2.3. At temperatures of 30°C (approximately the highest temperature attained in Britain), the expanding clay minerals will retain their interlayer water and there will be water molecules associated with the external surfaces of all clay minerals. In most agricultural situations a clay will present itself as an hydrated colloid surrounded by a swarm of cations.

2.3. INTERACTIONS BETWEEN CLAYS AND ORGANIC COLLOIDS

Negatively charged organic colloids would be expected to be repelled by the negatively charged clay minerals with little or no adsorption. This has been reported by several workers (Arlidge and Anderson, 1962; Law and Kunze, 1966). Since the anionic nature of organic acids depends on the hydrogen ion concentration of the system, the adsorption process of organic acids would be expected to be pH dependent. Thus, Bingham et al (1965) found acetate adsorption on montmorillonite to be greatest at low pH and least at high pH.

A large amount of experimental work has been carried out studying the adsorption of simple organic compounds, with known structures (such as acetate and amino acids), to obtain information concerning the bonding mechanisms involved. A related topic which has received attention is the interaction of clay minerals with organic pesticides. This subject has been reviewed by Bailey and White (1970). The herbicides paraquat and diquat, which are cationic quaternary bipyridyl compounds may be adsorbed onto clays by ion ex-

change processes. Weber et al (1965) studied the adsorption of paraquat and diquat by montmorillonite and kaolinite, and found that they are preferentially adsorbed up to their cation-exchange capacity. Bioassay studies have revealed that when pesticides are strongly adsorbed, they exhibit very little phytotoxicity. This apparent removal of the compounds from the soil-plant environment can be of great significance in agriculture and horticulture.

When simple organic materials do exist in the soil, they tend to be protected by adsorption or some other means. If not, compounds such as amino acids, organic acids and simple carbohydrates, would be utilised by soil microorganisms and disappear from the soil environment. Such compounds form a relatively small percentage of the total organic matter content of soil compared with the more complex, organic polymers. As the organic polymers have been shown to have an important effect on many soil properties, their interaction with clay colloids will be considered along with the mechanisms thought to be involved in clay-organic interactions.

2.3.1. Bonding Mechanisms at Clay Surfaces Involved in Soil Aggregation

Most theories that are put forward to explain the mechanisms of aggregation involve the concept that organic compounds form bonds with surfaces of clay particles. This interaction between clay and organic compounds may result in the formation of relatively stable aggregates through certain organic compounds bridging between neighbouring clay particles. Other clay-organic interactions result in the protection of the organic compound from biological degradation. Also biologically active compounds such as herbicides and insecticides may be adsorbed by clay minerals and rendered inactive; they

may later be released to become reactive or be degraded at the clay surface.

Two different approaches have been used in studying clay-organic complexes. The first was to allow various extracts and derivatives of organic matter to react with clays and to study the properties of the resulting complex. The other approach was to utilise organic compounds of known constitution and to deduce the nature of their interaction with clays from their known properties. The latter approach has resulted in considerable fundamental knowledge about the binding mechanisms involved between various functional groups of organic molecules and the clay mineral surfaces.

Polymers are strongly adsorbed by clay materials. The specific mechanisms involved in this interaction depend mainly on the chemical constitution of the polymer and the nature of the adsorbant surface. Other factors such as polymer molecular weight and flexibility, exchangeable cation, surface charge density, solvent and structural state of adsorbant (dispersed or aggregated) influence polymer adsorption.

The interaction between organic polymers and clay materials and the mechanisms have been extensively reviewed by Greenland (1965a) and Mortland (1970).

2.3.1.1. Cationic

(a) Ion exchange

Organic cations will be taken up at clay mineral surfaces by ion exchange with cations neutralising the negative electrical charges responsible for the cation exchange capacity of the mineral:

$$RNH_3^+ + M^+ - \text{clay} \rightleftharpoons RNH_3^+ - \text{clay} + M^+$$

where RNH_3^+ is an organic cation and M^+ another species of cation.

(b) Protonation of organic molecules at clay surfaces

Many compounds may become cationic after adsorption at the clay surface through protonation. The sources of protons are; (i) exchangeable H^+ occupying cation exchange sites, (ii) water associated with metal cations at exchange sites, or (iii) proton transfer from another cationic species already at the clay surface.

$$RNH_2 + H^+ - \text{clay} \longrightarrow RNH_3^+ - \text{clay}$$

where R is an alkyl group.

The second process by which organic molecules may become protonated is by proton donation from water at the clay mineral surface. Ordinary water is not likely to be acidic enough to protonate many organic molecules. However, when water is associated with metal cations, hydrolysis of this complex produces more or less H^+, depending upon the properties of the metal ion involved. A more electronegative metal cation (e.g. Al^{3+}) will form a more acidic, aqueous solution, than a less electronegative metal cation (e.g. Na^+). Therefore it would be expected that the ability of a clay surface to protonate compounds would be dependent upon the nature of the metal cations saturating the exchange sites on the clay. This has been shown to be the case by Russell (1965) and Mortland and Raman (1968).

(c) Hemi-salt formation

When the amount of an adsorbed base (B) on a clay exceeds the number of protons available for cation formation, one of the following situations occurs: (i) the protonated molecule retains its proton against attraction by the non-protonated molecule; (ii) two molecules compete for the proton on an equal basis, and it does not identify with either one but belongs to both, forming a strong,

symmetrical hydrogen bond and a cation of the $[B_2 - H]^+$ type.

(d) Cation bridging

Negatively charged compounds are not readily adsorbed onto the negatively charged surfaces of clay minerals, because of electrostatic repulsion. Several workers (Meyer, 1935; Peterson, 1947; Greenland, 1965a) have suggested that significant adsorption can occur through a polyvalent exchangeable cation.

For example, calcium (Ca^{2+}) could satisfy a negative charge on a clay mineral particle and the negative charge of a functional group of an organic polymer, thus acting as a bridge between the two colloidal particles. Iron (Fe^{3+}) could act in a similar manner to calcium or, because it is three valent, there is a possibility of iron that is a structural component of an organic polymer satisfying one negative charge at the clay surface. Yet another possibility could be an organic polymer satisfying the positive charge of a Fe^{3+} at the surface of an oxide particle. In this case the organic polymer would be in direct contact with the iron oxide.

2.3.1.2. Anionic

While anions are normally expected to be repelled from the surface of the negatively charged clay minerals, their presence at the clay surface has been observed (Yariv et al., 1966) indicating the presence of positively charged sites on the colloids. As the number of these positive sites only forms a small proportion of the total cation-exchange capacity, anionic exchange reactions are not likely to be of major importance.

2.3.1.3. Ion-dipole and Coordination

The classical view of adsorption of polar but non-ionic organic molecules by clay minerals has been to attribute a major

function to the oxygen atoms or hydroxyl groups of the silicate surface. This idea has developed mainly as an extension from earlier concepts of the mode of water adsorption at clay mineral surfaces as being mainly one of hydrogen bonding between oxygen atoms of the silicate surface and the water molecules.

With the advent of infra-red absorption techniques, it has often been possible to observe the condition of the adsorbed molecule directly, and to sometimes draw relatively unambiguous conclusions regarding the mechanisms by which they are held at the clay mineral surface. From studies of a large number of polar molecules adsorbed on clay minerals, it is evident that the saturating cation on the exchange complex plays a decisive role in the adsorption process. This was evident in the section on protonation (2.3.1.1(b)), where it was stated that the kind of exchangeable cation, with its associated water molecules, determined the acidity of the clay surface and therefore protonation processes. Also they serve as adsorption sites for polar non-ionic molecules by ion-dipole or coordination types of interaction (McNeal, 1964; Bissada et al,1967; Dowdy and Mortland, 1968). The greater the affinity exchangeable cations have for electrons, the greater will be the energy of interaction with polar groups of organic molecules capable of donating electrons. Thus, transition metal cations on the exchange complex having unfilled orbitals will interact strongly with electron donating groups.

2.3.1.4. Hydrogen Bonding

While hydrogen bonding is less energetic than Coulombic interactions, it is an extremely important bonding process in many clay organic complexes, being particularly significant in large molecules

and polymers because of the large number of hydrogen bonds which can be formed:

(a) Water bridge - involves the linking of a polar organic mole- to an exchangeable metal cation through a water molecule in the primary hydration shell.

(b) Organic - organic hydrogen bonding. When the exchangeable cation on the clay is an organic cation, the possibility exists of the interaction with another species of organic compound through hydrogen bonding.

(c) Clay mineral oxygens and hydroxyls. Hydrogen bonding of molecules with oxygens or hydroxyls of the clay mineral surface has been considered to be the primary mode of interaction and the basis for many models of adsorption.

2.3.1.5. Van Der Waals Forces

Van der Waals or physical forces operate between all atoms, ions or molecules, but are relatively weak. They result from attraction between oscillating dipoles in adjacent atoms, and decrease very rapidly with increasing distance between the interacting species.

2.3.1.6. Pi Bonding

Certain types of unsaturated hydrocarbons and their derivatives can be bound to the transition metals on the clay surface. These complexes are formed through the donation of π electrons of the organic compound to the α orbital of the transition metal. These metals could be present on the cation-exchange sites of the mineral, or present as substituted metals (Fe^{3+}, Co^{2+}, etc.) at the broken edges of the tetrahedral and octahedral sheets.

2.3.1.7. Entropy Effects

It has been proposed that the adsorption of some organic

polymers from solution onto clay minerals is favoured if there is a positive entropy change in the system (Greenland, 1972). When an organic polymer is adsorbed initially there will be a few points of contact with the clay surface. The theory proposes that when the molecule is strongly adsorbed a large amount of previously adsorbed water molecules is released from the clay surface. The gain in entropy by releasing these water molecules is much greater than the loss of entropy when the organic molecule is strongly adsorbed, which prevents free-rotation of the polymer segments. Therefore there is an entropy effect favouring the adsorption of the polymer.

2.3.1.8. Covalent Bonding

It is possible to create bonding between silicates and organic groupings by special techniques in the laboratory. For example, $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{C}}-$ type bonds can be formed by reacting acid anhydrides with silicates; the possible site of attachment being the exposed hydroxyl groups. Although this is unlikely to be an important mechanism, it has been suggested that this type of reaction could occur, naturally under the high pressures and temperatures to which minerals may be subjected.

2.3.2. Adsorption of Organic Polymers

Early work on the adsorption of linear, flexible, uncharged organic polymers at planar surfaces (Frisch and Simha, 1954; Frisch, 1955) suggested that they were adsorbed by a few "anchor segments" with most of the polymer chain extending into the liquid phase. Subsequently Silberberg (1962) suggested that in many instances the polymer was held to the surface by a large proportion of its segments, and the depth of the adsorbed polymer layer was considerably less than Simha et al (1953) had envisaged. His idea (Silberberg, 1962a, b, 1967, 1968) that half or more of the segments might commonly be

involved as anchor segments has been confirmed and extended by several investigations (Di Marzio and McCrackin, 1965; Roe, 1965; Montomura and Matuura, 1969).

These workers discuss the adsorbed polymer in terms of "trains"-sequences of segments all in immediate contact with the surface - "loops" - sequences of segments not in contact with the surface - and "tails" a sequence of segments leading to the end group, and none of which is in contact with the surface (Greenland, 1972). Two groups of polymers used extensively in the accumulation of experimental data are poly(vinyl alcohols) and poly(ethelyene glycols). Many investigations have studied the adsorption of these alcohols by montmorillonite (Greenland, 1963; Emerson and Raupach, 1964; Dowdy and Mortland, 1968; Parfitt and Greenland, 1970a).

The behaviour of polyelectrolytes is more complex than that of uncharged polymers, because their shape and other properties are more strongly influenced by pH and electrolyte concentration. If humic molecules were relatively compact spheres it is unlikely that they would be adsorbed onto clay mineral particles by physical adsorption forces alone (Greenland, 1965b). In fact it is expected that they would be repelled from the largely negatively charged clay surfaces. However, ultrasonic dispersion in clay liquids separates only a small proportion of the humic substances from the mineral part of the soil (Greenland and Ford, 1964). Presumably the humic substances are held by positive sites on the clay particles, or on hydroxy-aluminium oligomers or polymers, or by "bridge-linkages" involving polyvalent cations.

X-ray studies have shown humic substances do not penetrate

the interlamellar regions of expanding layer silicates or do so only with difficulty (Evans and Russell, 1959; Scharpenseel, 1966; Parfitt and Greenland, 1970b) unless the pH of the medium is taken to pH 4 (Schnitzer and Kodama, 1966; Evans and Russell, 1959; Martin and Reeve, 1960). In common with the behaviour of naturally occurring and synthetic polyanions (Reuhrwein and Ward, 1952; Lynch et al, 1957; Mortenson, 1962), humic substances are at best only weakly adsorbed by layer silicate minerals containing monovalent cations (Evans and Russell, 1959; Scharpenseel, 1966). Adsorption is increased by reducing the pH and/or raising the electrolyte concentration of the system (Evans and Russell, 1959) and by saturating the clay with polyvalent cations (Scharpenseel, 1966).

Enhanced adsorption in the presence of polyvalent cations is ascribed to the formation of a "cation bridge" which involves the displacement of a water molecule in the primary shell of the exchangeable cation by an anionic group of the humic acid (Greenland, 1971). Hydrogen bonding of the anion to a water molecule of this type may also occur. In fact, bonding by such a "water bridge" is the more common mode of linkage between polar organic molecules and clay mineral surfaces (Mortland, 1970; Theng, 1974).

When iron and aluminium occupy exchange positions at the clay surface additional types of bonding are possible. These ions can readily form polyhydroxy complexes (Greenland, 1971; Perrot et al, 1974) which acquire a positive charge at pH <8 so that anions may adsorb on them by electrostatic ("anion exchange") interactions.

Evans and Russell (1959) and Martin and Reeve (1960) have shown that there is no adsorption of humic substances by sodium montmorillonite unless the clay is first made acid and aluminium

enters the exchange sites. Flaig and Beutelspacher (1951) consider that their electron micrographs of mixtures of montmorillonite and humic acids show that an association between these two occurs through the intermediary of aluminium (or iron) oxides. Evidence supporting this suggestion was provided by the following observations: (1) Larger amounts of humic substances are adsorbed when iron and aluminium are present on the exchange sites (Martin and Reeve, 1960; Martin, 1960; Kobo and Fujisawa, 1963). (2) Humic substances are readily adsorbed by freshly synthesised iron and aluminium oxides (Schnitzer and Skinner, 1964). The exact manner in which humic substances are bonded to the aluminium or iron oxide has not been established; ionic interaction, co-ordination or chelation could be involved.

2.4. SOIL AGGREGATION

Soil structure is strictly a field term used for describing the overall arrangement or aggregation of the soil solids. Structure has been defined as "referring to the arrangement of the solid particles in the soil profile" (Bradfield, 1950; Low, 1954; Marshall, 1962). By this definition there is no such thing as a structureless soil, any process which alters the arrangement of the solid particles is altering the structure of the soil.

Four types of soil structures are generally recognised (see Figure 4):

(i) Platelike. In this structural type the aggregates or groups are arranged in thin horizontal plates or leaflets.

(ii) Prismlike (columnar and prismatic sub-types). These sub-types are characterised by vertically orientated aggregates or pillars which vary in length with different soils. When the tops are rounded, the term columnar is used to describe them and when the

tops of the prisms are level and clean cut the aggregates are designated prismatic.

(iii) Blocklike (blocky and sub-angular blocky sub-types). Aggregates have been reduced to blocks, irregularly six-faced with their three dimensions roughly equal. When the edges of the cubes are sharp and the rectangular faces distinct the aggregates are referred to as blocky. If sub-rounding has occurred the type is designated sub-angular blocky.

(iv) Spheroidal (granular and crumb sub-types). These two types of rounded aggregates are distinguished by the term crumb being applied to especially porous aggregates.

The term aggregation refers to the combination of the primary soil particles (sand, silt and clay) in varying proportions to form larger entities, called soil aggregates. The size of aggregates can vary from half a millimetre to many millimetres in diameter. The process of soil aggregation is generally thought to involve two sets of factors: (a) those responsible for aggregate formation, and (b) those responsible for the stabilisation of the aggregate once it has formed. Since both sets of factors and the processes or materials responsible for them are acting simultaneously it is difficult to separate their relative effects on the development and production of stable aggregates in the soil.

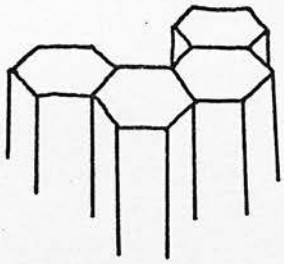
Soils under permanent grassland are often found to be well aggregated, generally having a granular structure (Low, 1954). In such a soil there are large pores between the aggregates which allow excess water to drain away under the force of gravity, and permit oxygen and carbon dioxide to diffuse in and out of the soil freely. Also within the aggregate are smaller pores that retain water against

Figure 4. Types of Soil Structure

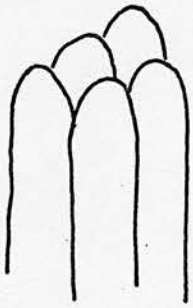
1. Platelike

horizontal plates, leaflets or lenses

2. Prismlike



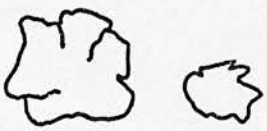
prismatic (level tops)



columnar (rounded tops)

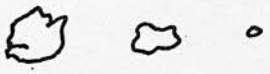
3. Blocklike

blocky (cubelike)



subangular blocky

4. Spheroidal



granular (porous)

crumb (very porous)

natural drainage, which is then available for uptake by plant roots. The same soil cultivated continuously might well have a different type of soil structure, such as platy or blocky units. This can give rise to a poorer soil structure leading to problems such as waterlogging, plough pans, capping, etc. which reduce the soils potential for crop production.

The type and stability of aggregates formed in a given soil are determined by many factors including climate, vegetation, soil type, soil organisms, soil components and farming practice.

2.4.1. Vegetation

The influence of the vegetation on soil aggregation is a reflection of the combined effects of diverse physical, chemical and biological agencies. The relative contribution of these agencies to the formation and degradation of soil aggregates varies with different cropping systems.

A great deal of work concerning the role played by crops in soil aggregation has involved investigations into the effect of the massive network of roots which permeate the soil (e.g. Kolodny and Neal, 1941). The pressure exerted by actively growing plants has been associated with both the formation and breakdown of aggregates. Root penetration into large aggregates may cause a separation of aggregated soil particles, while individual sand, silt and clay particles may be trapped inbetween the network of plant roots and associated mycelia, and aggregates formed (Hubbell and Chapman, 1946).

There is also the suggestion that growing roots may secrete substances which act as soil binding agents. If these substances are not capable of binding soil particles together to form aggregates, microorganisms could be involved in converting plant-root secretions

and/or sloughed-off residues into soil binding agents (Stallings, 1953).

The decrease in soil aggregation following the cultivation of grassland and the improvement of aggregation caused by the introduction of grass leys attest to the aggregating efficiency of continuous grass (Gish and Browning, 1948; Olmstead, 1946; Browning, 1937; Low, 1954). However several workers (McHenry and Newell, 1947; Ward, 1949) reported that different grass species have different aggregating effects. For example Pringle and Coutts (1956) found that timothy was more effective than ryegrass, cocksfoot and red fescue in improving aggregation; meadow fescue had only a small effect.

Russell (1938) noted that vegetation is important in protecting surface aggregates from degradation due to climatic agencies. This is especially the case for soils in which capping can occur after a heavy rainfall.

2.4.2. Soil Organisms

The definition of a soil organism is that it spends at least some part of its life cycle in the soil medium. Members of the following groups of invertebrates fall into this category:- Nematoda, Annelida, Mollusca, Crustacea, Myriapoda, Insecta, Arachnida and Protozoa (Russell, 1923). These organisms together with algae, fungi and bacteria are responsible for the conversion of plant and animal tissue into new organic compounds, some of which are incorporated into their body tissue and some are released back into the soil matrix. The phytophagous and saprophagous species of invertebrae are often prominent in the initial stages of decomposition.

Although the insects form the dominant element in the invertebrate fauna it is the earthworm that has received the most attention in connection with soil aggregate formation. The importance of earthworms in the improvement of soil structure is evidenced by the comminution of mineral particles, dissemination of microorganisms, creation of water-stable aggregates, and their burrowing activity whereby aeration, drainage and water retention are enhanced (Kühnelt, 1976).

Whether earthworms without the aid of microorganisms are responsible for stable aggregate formation has not been determined. Work by Hopp and Hopkins (1946) showed that incubation did not stimulate microbial activity and increase aggregation. Conversely, Finck (1952) found wormcasts contained many times more bacteria than the surrounding soil and Swaby (1949) attributed greater stability of grassland wormcasts to gum producing bacteria that cemented casts into stable aggregates.

Many investigations have been carried out to try and determine the effect of bacteria and/or fungi on the decomposition of organic material. In such an experiment, Gilmour et al (1948), McCalla et al (1957) and Martin et al (1959) incorporated organic residues, possessing little or no innate soil binding power, to soil and invariably found that in the presence of microorganisms (but not in their absence) soil aggregation was improved after incubation. Martin and Waksman (1941) found that the extent and the time required for aggregation to reach a maximum depended upon the nature of the soil, the type of organism concerned and the chemical nature of the organic material used.

Diverse species of bacteria, fungi, streptomycetes, yeasts

and algae are capable of binding soil particles into stable aggregates. However the ability of organisms to aggregate soils differs widely. McCalla (1946) and Swaby (1949) in separate investigations decided on the same general order of importance of these organisms:- Fungi > streptomycetes > gum producing bacteria > yeasts > other bacteria. Presumably the efficiency of a mixed culture of organisms in forming stable aggregates depends on mutual compatibility and the extent of competition for food.

2.4.3. Climate

Climate plays a major role in determining the effects of vegetation, organisms, cultivation and soil conditions on aggregation. Climatic-dependent variables, such as moisture and temperature, play a direct role in the formation and destruction of soil aggregates.

Much experimental work has been performed in an attempt to discover the role played by wetting and drying and/or freezing and thawing in aggregate formation and stabilisation. The resulting reports have been conflicting; Rost and Rowles (1941) and Slater and Hopp (1949) found no change in aggregate stability, whereas other workers (Russell, 1950; McHenry and Russell, 1944; Willis, 1955) claimed that these agencies increase stability. Even if these processes do not actually form aggregates, the physical movement of soil particles as the soil matrix freezes and thaws or wets and dries might allow the particles to be orientated in such a position so that aggregation can occur.

In arable cropping systems rainfall can have an important effect on soil aggregates when there is no crop cover. In a study on raindrop energy and soil erosion, Ellison (1952) stated that the force of raindrops beating on bare ground damages the soil by breaking

down their crumbs. Breakdown of the soil aggregates together with compaction and deposition of fine particles at the surface results in the formation of a soil crust. Many workers (Hank and Thorp, 1957; Lemos and Lutz, 1957; McIntyre, 1958) have studied surface crusts and the adverse effects they can have on seedling emergence. It has also been shown that the size of the raindrops markedly affects crust strength (Sale, 1964; Bean and Wells, 1953); small drops have little effect at all, but large drops being harmful to surface structure.

The state of aggregation at any given time of the year is a function of aggregate formation and degradation processes. In general the number of stable aggregates increases in the spring to a maximum in summer and then decreases throughout the autumn to a minimum in winter (Henin, 1939; Alderfer, 1950; Rennie et al, 1954). Increased aggregation in spring is associated with a high production of aggregating agents of microbial origin due to favourable conditions for microbial activity.

2.4.4. Soil Constituents Involved in Aggregation

The diversity of soil constituents implicated in aggregate formation, degradation and stabilisation has given rise to a great number of investigations. Clay, humic substances, polysaccharides, aluminium, iron and calcium have all been proposed in the past fifty years as soil constituents which stabilise soil aggregates.

2.4.4.1. Iron and Aluminium

Mineral soils contain varying amounts of polymerised iron, silica and aluminium iron hydroxides which are amorphous in structure. These amorphous hydroxides make up only a small proportion of the soil mineral matter, but because they are deposited on surfaces and are

chemically reactive, they are of great importance in certain soil processes. Lutz (1936) and Kemper and Koch (1966) found a close relationship between the amount of free oxides and aggregate stability; but no similar relationship was found for aluminium oxides. Schahabi and Schwertmann (1970) treated soil with a solution of iron hydroxides and showed that this increased its wet-sieving index.

Desphande et al (1968) compared the effectiveness of specific extraction of iron hydroxides, aluminium hydroxides and carbohydrates on the stability of Australian soils. They found that iron hydroxides appeared to exist in discrete particles and were not important binding agents, but some evidence was found suggesting cementing action by aluminium. Giovaninni and Sequi (1976) found a correlation between aluminium, as well as iron, and water stability of soil aggregates. They proposed that the iron and aluminium are part of a polymeric chain of soil organic matter which is part of a mesh or net that exerts a protective action on soil aggregates, and that removal of iron and aluminium weaken the net and reduce stability. It has also been proposed that amorphous metal hydroxides could stabilise the polysaccharide bridges between soil particles through the formation of a coating of insoluble complexes.

2.4.4.2. Calcium

Although Kemper and Koch (1966) concluded that calcium is not directly responsible for improving soil aggregate stability, several workers (e.g. De Boodt et al, 1961) have stated that additions of calcium to soils increases aggregate stability. It is well known that the nature of the ions on the cation exchange sites play an important role in determining the dispersion or flocculation behaviour of clay part-

icles. For example, if sodium is a prominent ion on the exchange sites, the soil particles may disperse and a very undesirable soil structure can result. A predominance of calcium by contrast may encourage a phenomenon called flocculation. When this occurs, the colloidal matter is brought together in floccules which can then be stabilised or aggregated by other agencies.

2.4.4.3. Clay

Martin et al (1955) proposed that clay is the predominant binding agent in soil aggregation, and that organic materials do not act primarily to hold clay, silt and sand grains together, but rather their chief role may be to modify forces by which clay particles are attracted to one another. It was suggested that cohesive forces between clay particles may involve: (i) linkage by chains of water dipoles, (ii) bridging between clay particles by polar long-chain organic molecules, and (iii) cross-bridging and sharing of inter-crystalline ionic forces and interactions of exchangeable cations between orientated clay plates.

Russell (1961) stated that clay forms a continuous network in most soils that enmeshes and may bind silt and sand particles together. The exchangeable ions and charges on the surface of clay particles interact with water molecules between the surfaces; the binding forces increase as neighbouring clay particles assume preferred orientations. Therefore any process conducive to providing preferred orientations is helping to increase the aggregate stability.

One such natural process is the swelling and shrinking action of the 2:1 clay minerals, which have an expanding lattice. This movement of particles relative to each other would greatly improve the chances of getting the necessary orientation, for the formation

of clay-organic complexes. The expanding lattice clays, such as vermiculite and montmorillonite, also have a much higher cation-exchange capacity than clays with a fixed lattice (section 2.2.2.), e.g. kaolinite and illite. These properties make the expanding lattice clays potentially more capable of forming stable soil aggregates.

2.4.4.4. Organic Material

Most theories concerning the role of organic matter in soil aggregation involve the concept that organic compounds form bonds with the surfaces of one or more clay particles rather than forming a matrix around the soil particles. Robinson and Page (1950) postulated that organic matter promotes aggregate stability by (i) reducing aggregate swelling, (ii) decreasing aggregate wetability, (iii) reducing the destructive forces of entrapped air, and (iv) increasing the inherent strength of the aggregates.

The role of organic matter and/or its sub-fractions in forming and stabilising soil aggregates has received a great deal of attention; this work was dealt with in section 2.3.

(a) Polysaccharides and soil aggregation

Approximately 5-16% of the soil organic matter is in the form of carbohydrates (Waksman and Stevens, 1930; Gupta et al, 1963). Microorganisms play an important role in the carbohydrate cycle. Bacteria, actinomycetes and fungi are chiefly responsible for decomposing plant and animal remains. These microorganisms then synthesise polysaccharides and other carbyhydrates in their cells, frequently as major metabollic products.

A large proportion of soil polysaccharides can only be recovered after harsh treatment of the soil with chemicals (e.g.

concentrated sulphuric acid). Therefore, great difficulty is experienced in isolating them in the exact form that they exist in the soil, because of the changes that might occur during the extraction.

The role of microbial polysaccharides in the formation of stable soil aggregates has been the subject of investigations extending over many years. The presence in the soil of gum-like polysaccharides which are capable of bringing about aggregation has been demonstrated by many workers (Acton, et al, 1963; Forsyth, 1950; Rennie et al, 1954; Whistler and Kirby, 1956) and there are good grounds for believing that these substances are of microbial origin (Forsyth, 1950; Keefer and Mortenson, 1963). Further, there are a number of studies which show a good correlation between the levels of "microbial gum" and aggregation (Acton et al, 1963; Chesters et al, 1957).

Despite this evidence there are many objections to the "polysaccharide theory" of soil aggregation. Relationships between soil polysaccharides and aggregation are certainly more complex than was formerly envisaged (Swincer et al, 1969) and in certain soils (e.g. old grassland and forest soils), they do not appear to play any significant role (Greenland et al, 1964; Griffiths and Burns, 1972; Mehta et al, 1960). Where soil polysaccharides do appear to exert an influence on soil aggregation, as for example in young grass leys (Greenland et al, 1964), the effects are ephemeral (Low, 1954; Low et al, 1963). This behaviour accords well with the ease with which polysaccharides can be degraded by other soil microorganisms (Harris et al, 1963; Martin et al, 1959; McCalla, 1946).

Laboratory experiments, in which polysaccharide additions increase stability of soil aggregates do not necessarily establish

that the same mechanisms of aggregate stabilisation occur in natural aggregates. Some evidence for the role of polysaccharides in aggregation is the loss of stability brought about by the treatment of natural aggregates with dilute periodate followed by borate solutions, and pyrophosphate solutions. The common stabilisation mechanism disrupted by these chemicals is thought to be the polyuronide-polyvalent cation bridge (Stefanson, 1971). This treatment, which is reported to have little effect on other materials, confirms that in many soils polysaccharides play a major role in the formation of stable aggregates (Greenland et al, 1962; Harris et al, 1963; Clapp and Emerson, 1965).

However, attempts to ameliorate poor structure by the addition of naturally occurring polysaccharides in field situations have not been successful for the following reasons (Hendrick and Mowry, 1952).

(i) The large amounts (5-10 tons/acre) required to give significant improvement in structure cause harmful effects through the release of large numbers of cations into the soil (whether sodium, potassium or ammonium).

(ii) The large quantity of readily decomposable organic material introduced causes denitrification, and at least temporary unavailability of other plant nutrients.

(iii) The rapid decompostion of added polysaccharide derivatives by soil microorganisms (2 weeks - 2 months) renders such methods uneconomical.

(b) Other non-humic substances and soil aggregation

Hydrophobic soil organic components, such as fats, waxes and resins, have been implicated in aggregate stabilisation (Henin, 1944; Geoghegan, 1950; Bond and Harris, 1964; Harris et al, 1966).

In this context the main role of these compounds probably lies in preventing the entry of water into preformed aggregates rather than in an actual binding of the aggregate constituents. Henin et al (1958) suggested the pretreatment of aggregates with benzene prior to sieving to differentiate between aggregate stability caused by particle-binding substances and substances which act merely to reduce soil wettability.

The relationship between amino acids or proteins and soil aggregation has not been studied. Many workers (Giesking, 1939; Hendricks, 1941; Esminger and Giesking, 1941; Estermann et al, 1959; Armstrong and Chesters, 1964; Greenland et al, 1965; Greenland, 1965b) have shown that both cation-exchange and physical adsorption forces are involved in the adsorption of both these compounds by montmorillonite. This work originated because the hypothesis that proteins constitute a large proportion of the organic matter was untenable unless some mechanism could account for the fact that they were not broken down by microorganisms.

Griffiths and Burns (1972) studied the effect of additions of tannic acid on the stability of soil aggregates. The results showed that tannic acid incorporated into the soil before moulding soil aggregates had little effect on aggregate stability, but when applied to moulded aggregates there was a rapid increase in stability, followed after three weeks, by an equally rapid decline. An addition of tannic acid plus polysaccharide material also gave an immediate increase in stability, but the stability lasted for the duration of the experiment (four weeks). They also made additions of benzoic acid, catechol, o-coumaric acid, gallic acid, phloroglucinol, pyrogallol and resorcinol to soil and studied their effects on aggre-

gate stability. They found that only pyrogallol and resorcinol gave small increases in aggregate stability. From this work Griffiths and Burns (1972) suggested that phenolic compounds and polysaccharide material acting together could be responsible for stabilising soil aggregates.

(c) Humic substances and soil aggregation

Very little work has been undertaken studying the effect of humic substances on the stabilisation of soil aggregates. Harris et al (1966) stated that adsorption of colloidal iron oxides and humus is essential for satisfactory soil structure. Sideri (1936, 1938) visualised soluble humates being orientated on clay particles, thus forming films. On drying these films are irreversibly dehydrated and cement particles into stable aggregates. Aleksandrova and Nad (1958) pointed out that humic substances are precipitated when iron and aluminium replace hydrogen ions, and surface precipitation on clays may occur. Drying of the clay-organic complex leads to the formation of a condensed film not readily removed.

Gedroits (1955) suggested two distinct stages in soil aggregation: a) coagulation of soil colloids under the influence of calcium ions to form primary microaggregates, and b) cementation of the microaggregates into macroaggregates by highly dispersed organic substances.

Tuilin and Kosovkina (1950) and Tiulin (1954) distinguished two main groups of microaggregates according to the mode of formation and the nature of the bonding material. Group 1 microaggregates, stabilised by calcium humates, were formed outside the rhizosphere and were characterised by relatively low amounts of sesquioxides and organic matter. Group II microaggregates, stabilised by iron

humates, were formed principally under the influence of the rhizosphere-inhabiting organisms.

In the last twenty years a certain amount of work has been carried out on the adsorption of humic substances by specific clays (section 2.3.). While these studies have led to a partial understanding of the mechanisms involved in the adsorption process, very little information has been obtained concerning the effect of such interactions on soil properties. This is an area of study which deserves more attention from workers in this field.

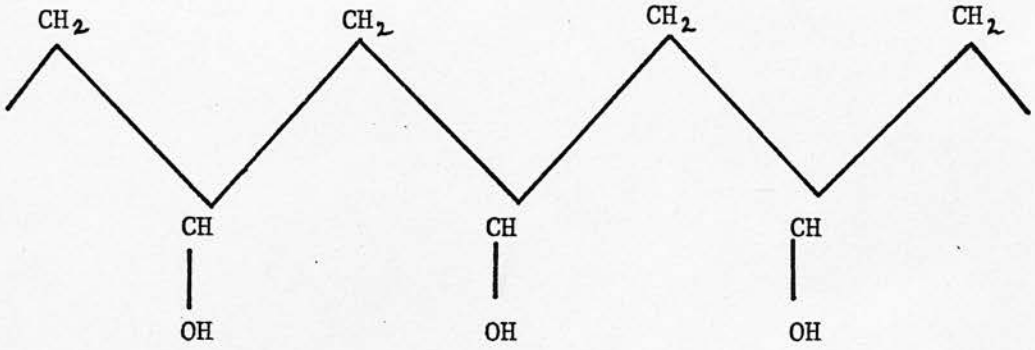
(d) Synthetic organic polymers and soil aggregation

In addition to carrying out experiments to investigate the effect of naturally occurring organic compounds (e.g. polysaccharides, fats, waxes, humic substances) on the aggregation of soil, many studies have been carried out using synthetic organic compounds. Examples of such compounds are polyvinyl alcohol (P.V.A.), carboxymethyl cellulose (C.M.C.), and krilium-related conditioners - such as vinyl acetate - maleic acid copolymer (V.A.M.A.), polycrylonitrile (P.A.N.), hydrolysed polyacrylonitrile (H.P.A.N.) (Figure 5). These compounds possess functional groups and properties similar to soil and microbial polysaccharides. Hence the mechanisms involved in aggregation by artificial polymers are probably similar to those of some natural soil polymers.

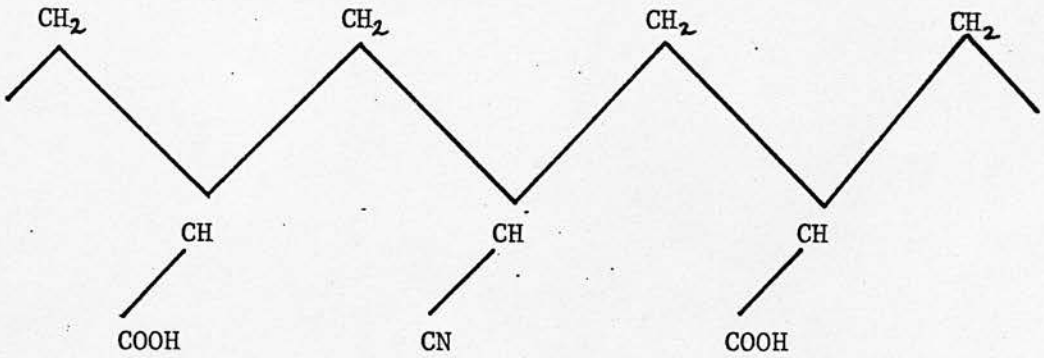
Extensive work was carried out in America during the 1940s, and by 1952 more than 700 chemicals had been screened for their effect on stabilising soil aggregates (Hendrick and Mowry, 1952). The ideal compound would need to be water soluble and effective at very low concentrations, for practical and economic reasons. Two such materials on which most work was done initially were C.R.D.-

Figure 5 Examples of Synthetic Organic Polymers which have been Studied in Relation to Soil Aggregation

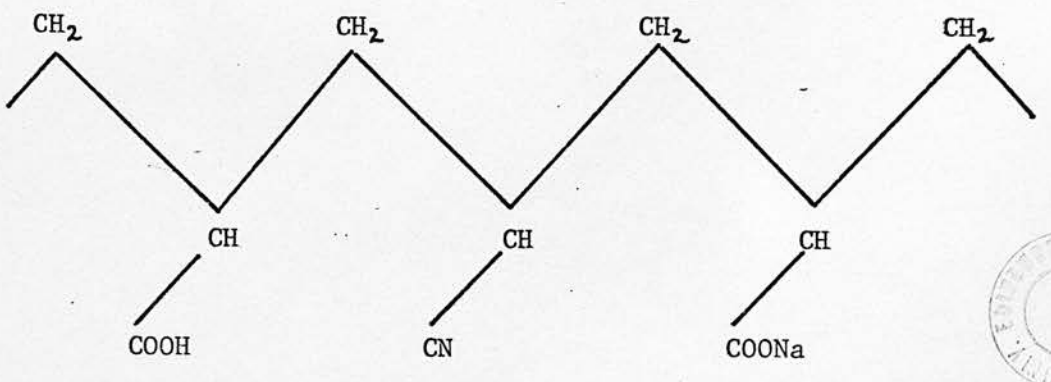
(a) Poly (vinyl alcohol). P.V.A.



(b) Poly (acrylonitrile). P.A.N.



(c) Hydrolysed poly (acrylonitrile). H.P.A.N.



189, the sodium salt of hydrolysed polyacrylonitrile, and C.R.D.-186, a carboxylated polymer. The biological breakdown of both C.R.D.-186 and C.R.D.-189 is negligible over a period of two years. These compounds are effective in concentrations of 0.01 to 0.1%, giving improved aeration, increased infiltration and percolation rate and a higher water holding capacity.

Martin et al (1952) used several of these synthetic polymers in field experiments, applying them at rates varying from 0.02 to 0.2% in powder form, with subsequent mixing. They found that although not all crops responded to the treatments, in many cases yields were increased appreciably. However, without exception, additions improved soil aggregation and related characteristics, such as porosity, of the heavy textured soils studied. These aggregates were water stable and the structural improvement persisted through the second growing season.

In fact many workers have found that the addition of polyelectrolytes, such as V.A.M.A. and H.P.A.N., resulted in an increase in water-stable aggregation (Raney, 1953; Weakly, 1960; Pugh et al, 1960; Simpson and Hayes, 1958; Taylor and Baldridge, 1954; Allison, 1956; Allison and Moore, 1956). Emerson (1956), Williams (1965) and Williams et al (1968) have also shown the uncharged polymer P.V.A. to be a very powerful stabilising agent. In addition emulsions of water-insoluble materials, usually bitumen, have been found to be effective in aggregating and stabilising coarse textured soils and pure sands (De Boodt, 1972; Gabriels et al, 1972).

2.5 THE EFFECT OF CROPPING SYSTEMS ON ORGANIC MATTER AND AGGREGATE STABILITY

Experiments have been carried out over a period of 20 - 30 years by four different research organisations studying the effects of ley and arable cropping systems. Factors which have been measured include:- organic matter content, nitrogen content, polysaccharide content, aggregate stability, crushing strength of air-dry aggregates, draw-bar pull during ploughing, soil respiration, water supply, effect of synthetic conditioners on crop yield, effect of fertilisers on crop yield.

Cooke (1967) stated that the value of the leys in the Rothamstead and Woburn experiments (Johnston, 1973) was almost entirely nutritional, the improvement in soil physical conditions due to leys being unimportant to succeeding crops. However, significant losses in the amount of carbon present have been observed since the start of the experiments; a 25% loss from Highfield (permanent pasture put into cropping) and 10% from Fosters field (continuous cropping).

In the A.D.A.S. ley fertility experiment (Eagle, 1971 and 1975; Myint, 1975) a three year ley maintained organic matter levels at three sites only. Whereas a nine year ley gave a marked accumulation, but this was lost in the subsequent three years of cropping at all but two sites. In general it was considered that the improvement in soil physical conditions after ley was unimportant compared with the residual nitrogen they provided.

The Jealotts Hill experiments (Low, 1975) were carried out on a sandy loam soil overlying clay, which had an inherently unstable structure. This lead to marked differences being observed

between the structural condition of soil in ley-arable and all-arable rotations. From long term experiments, Low(1975) concluded that under the soil and climatic conditions of Jealott's Hill, yields of cereals are not maintained without a grass break, even in the presence of adequate amounts of fertilisers.

The fourth set of ley-fertility experiments were carried out at the Grassland Research Institute, Hurley (Clement, 1975). The results showed that three to four years under leys increased both soil organic matter and water-stable aggregation, but not air-filled or water-filled pore space; perennial ryegrass having a greater effect than other grasses.

In an earlier study Clement and Williams (1959) found that the extent of water-stable aggregation in the top 2 - 3cm of a sandy loam arable soil, as determined by wet-sieving, was more than doubled after three years under ley. There were no marked changes in soil organic matter content or water-stable aggregation below 4cm. When the ley was ploughed for an arable crop, the top 3cm of soil was buried and material little affected by the ley was brought to the surface. Therefore the ley had no subsequent effect. Low et al (1963) also found that periods under ley increased the water stability of the air-dry soil aggregates. But he suggested that after two years of arable cropping, the effect of a 3yr ley is still apparent on water-stable aggregation. Whereas after two years of cropping, the effect of a 2yr ley has largely disappeared, and the effect of a 1yr ley has completely disappeared.

Studies have also been carried out examining the differences between the organic matter of grassland and arable soils. Garwood et al (1972) found that in a three year old grass sward the macro-organic matter (that retained on a 0.25mm sieve) accounted for

approximately half of the increase in soil carbon since seeding, and half or less of the increased nitrogen. Whitehead et al (1975) made organic matter and nitrogen measurements at arable and permanent pasture sites on a chalk soil. They found that there was a much greater proportion of the total in the light fraction (coarse organic matter) of grassland soils, than arable ones. Ford and Greenland (1964) obtained the light fraction from a number of Australian soils and suggested that it contained partly humified plant residues. The light fraction accounted for a large proportion of the total carbon and total nitrogen. In a later study (Ford and Greenland, 1968) they found that a large proportion of the nitrogen released on incubation was due to mineralisation of the light-fraction nitrogen.

With regard to carbohydrates, the data of Cheshire and Anderson (1975) suggests that the proportion of saccharides was the same for fallow and cultivated soils from Rothamstead. Whitehead et al (1975) found that the proportions of the soil organic carbon released by hydrolysis as neutral sugars, uronic acids, amino sugars and phenolic acids were generally similar for the three soils tested (continuous cultivation, 17yr grass after continuous cultivation and permanent grassland). Myint (1975) also found that, in general, leys had little effect on the relative proportion of material found in soil humus fractions (more than 10 fractions were examined), obtained from soils of the A.D.A.S. ley-fertility experiments.

The studies to date indicate that the organic matter formed under grass leys does not differ greatly from that under arable crops. The major effect of leys on soil organic matter would seem to be to increase the quantity of partially humified plant materials.

An improvement in soil aggregate stability is detectable in the top four centimetres after a two or three year ley. However, when the ley is ploughed for the subsequent arable crop, this 'improved' layer is buried, and any beneficial structural effect of the ley may be nullified.

2.6 EVALUATION OF SOIL AGGREGATE STABILITY

The stability of structure refers to the resistance that the soil aggregates offer to the disintegrating influence of various agencies such as water, chemical solutions and mechanical manipulation. During the last fifty years several methods have been put forward for assessing soil aggregate stability.

2.6.1. Stability against Disruption during Wet-sieving

This method has been employed by many workers who have studied aggregate stability, and consequently there are many modifications of the original procedure put forward by Tiulin in 1928 (e.g. Yoder, 1936; Russell and Feng, 1947; Kemper and Koch, 1966). Basically the apparatus consists of a nest of sieves oscillated in a vertical plane in a liquid medium, usually water. The mechanical action of the liquid causes unstable aggregates to breakdown into secondary particles, these are then collected on the finer sieves below or pass into dispersion. To obtain meaningful results using this method a large number of potential variables must be kept constant throughout the investigation. These include sieve size, sieve number, aggregate size, pre-treatment of aggregates, duration of sieving, number of oscillations per unit time, amplitude of oscillation and the liquid medium.

Treatment of soil aggregates prior to wet-sieving. Kemper and Koch (1966) decided that the time and means of sampling did not have a significant effect on results. However, Slater (1953) found that aggregate stability increased as the soil drying temperature increased from 4°C to 82°C, and Kemper and Koch (1966) showed that soils with a high exchangeable sodium percentage had high aggregate stabilities when dried at 105°C.

Many workers have found that if aggregates are maintained in an air dry condition for a long period of time stability increases with the length of time (De Leenheer and De Boodt, 1959). Also Yoder (1936) and Russell (1938) found that air drying decreases the percentage of large aggregates in favour of the smaller ones. Williams and Cooke (1961) stated that soil aggregates less than 0.5mm in diameter are stable, from 0.5-4mm instability increased rapidly with increasing size, and above 4mm there is little change in stability. They used 4-6mm aggregates in their investigations. Whereas Bryant et al (1948) used 3-5mm aggregates and Kemper and Koch (1966) used 1-2mm aggregates. It is generally accepted that soil samples should be air-dried and wet-sieving performed within two months on as small a range of aggregate size as is practicable.

However, there is less agreement about what is the best method of pretreating aggregates before wet-sieving. If air-dry aggregates are placed straight into water disruption occurs due to (a) forces exerted by air entrapped within the aggregates, (b) differential swelling in soil aggregates containing clay, and (c) the energy of hydration as soil particles go into dispersion. It is very important that this disruption or slaking of aggregates is kept to a minimum or the results obtained will not be a reflection

of breakdown caused by wet-sieving. Emerson and Grundy (1954) and Smith and Browning (1946) reported that the problem of aggregate breakdown due to entrapped air could be overcome by wetting the aggregates under vacuum. Other workers (Henin et al, 1955) have found that using ethyl alcohol as a wetting agent also obviates this effect. However, there is still disruption due to differential swelling especially in soils with a high clay content. Panabokke and Quirk (1957) recommend that aggregates should be wet to a water tension of pF 2 or 3 before wet sieving. Various methods have been put forward to attain this moisture tension such as wetting slowly by capillarity, enclosing the aggregates in a saturation chamber or using an atomizer.

Variables in the wet-sieving operation. Russell and Feng (1947) oscillated aggregates for different periods of time and found that aggregate stability decreased exponentially with time. Aggregates with high initial stabilities and low rates of disintegration were classified as the most stable. The choice of sieve size, length of sieving time, sample size, stroke length and frequency are all arbitrary and are usually chosen to suit the apparatus and soils to be used.

Expression of results. There have been attempts to express the data obtained by wet-sieving as a single representative figure such as the mean diameter of the aggregates at the 50 per cent level of the accumulation curve (Robinson and Page, 1950), the mean weight diameter (van Bavel, 1949) and the geometric mean diameter (Mazurak, 1950).

2.6.2. Stability against the Impact of Falling Drops of Water

The action of rain drops on aggregate disintegration is simulated in the water-drop method (McCalla, 1944; Low, 1954).

Stability is measured by the number of water-drops of a given diameter, falling from a certain height onto an aggregate of soil, that are required to completely destroy the aggregate. Wetting and swelling cause loosening of the lump and so enable drops to break it down.

2.6.3. Stability against Disintegration during Leaching with Dilute Sodium Chloride Solutions

Emerson (1954) measured the stability of soil aggregates by determining the concentration of sodium chloride that caused the aggregates to disperse and render them impermeable. Aggregates were leached with 0.5M sodium chloride solution to replace any exchangeable cations present. They were then percolated with increasingly dilute solutions of sodium chloride and changes in permeability noted. The concentration of sodium chloride solution which caused complete dispersion of aggregates and reduced permeability to zero, was used as an index of stability.

A modification of this experiment (Dettman and Emerson, 1959) required only one concentration of sodium chloride. This was chosen so that deflocculation was avoided in the case of "known" stable soils and produced a significant decrease in permeability of "known" unstable soils. An index of stability was obtained by calculating the ratio of the initial permeability of the aggregates to the final permeability.

2.6.4. Stability against Disintegration by Applying Water Tension

In a modification of Childs' (1940) moisture characteristic method, Ingram (not published) wetted soil aggregates and then applied increasing water tension. The change in porosity, which is obtained from a moisture characteristic curve, indicates the breakdown of aggregates. The stability index was calculated as the ratio

of percentage pores emptied between 0 and 10cm for the untreated and treated aggregates. An alternative method is to calculate the slope of the moisture characteristic and plot this against tension. The index is obtained from the ratio of the peak heights on the graph.

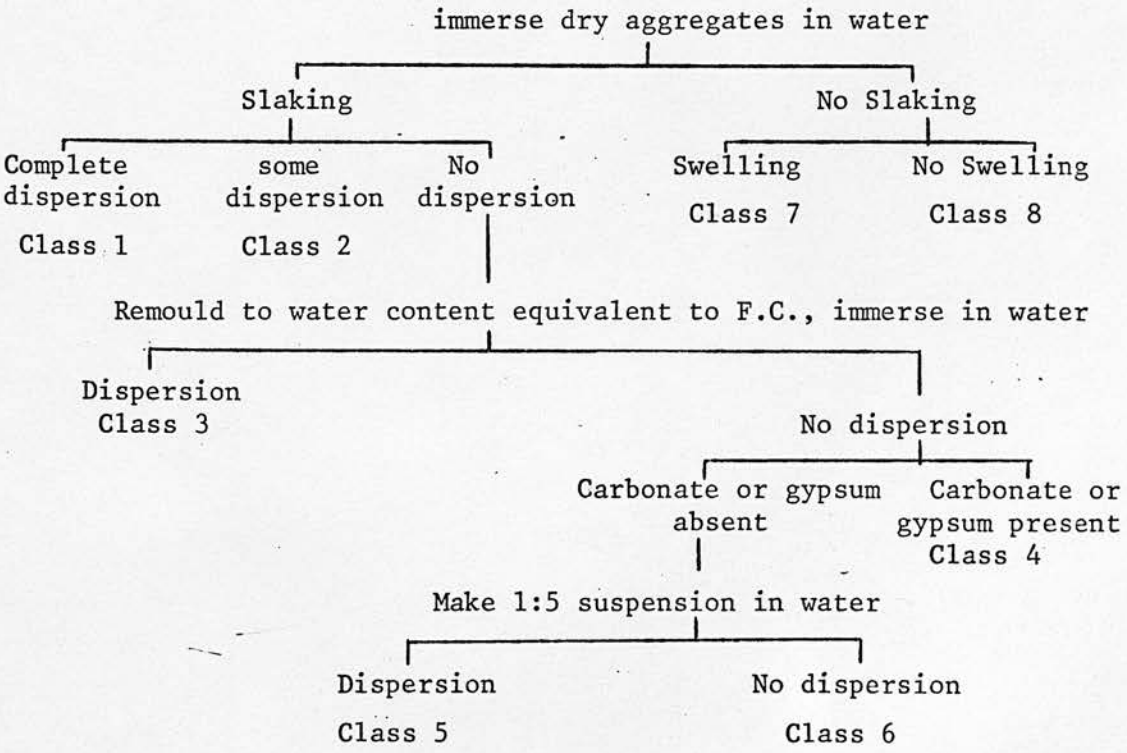
2.6.5. Stability Class from Slaking, Swelling and Dispersion Observations

Emerson (1967) proposed a classification of soil aggregates into eight classes based on the coherence of the aggregates in water.

Greenland et al (1975) modified this test and examined the structural stability of surface soils with the aim of distinguishing soils likely to have structural problems in the field (Figure 6).

Williams and Cooke (1961) obtained a measure of stability for air-dried aggregates (4-6mm) after two cycles of wetting and draining. This was basically a slaking test in which the percentage loss in pore space was taken as an index of structural instability.

Figure 6. Classification of aggregates according to cohesion in water



2.6.6. Liquid Limit Determined by the Cone Penetrometer as a Measure of Aggregate Stability

Liquid limit determinations of soils using a similar method to that described in BS 1377 (British Standards Institution, 1975) have been carried out by several workers (Sherwood and Ryley, 1970; Towner, 1973; Campbell, 1974). Towner (1973) suggested that cone penetrometer measurements could be used for characterising soil behaviour. Therefore, because of the relationship between soil organic matter and the liquid limit, it is possible that the cone penetrometer could provide an accurate method of obtaining an index of aggregate stability.

2.6.7. Absolute Measurement of Soil Structural Stability using Ultrasound

An absolute measurement of soil structural stability was devised by North (1976) using the controlled application of known dispersive energies derived from a calibrated ultrasonic probe. The method basically entails dispersing air-dry crumbs (<2mm), placed in a glass cell with 50mls of water, by irradiating the sample at different power levels. A graph plotting dispersive energy against percentage weight fraction <2μm gives the dispersion characteristic. The energy at which secondary disaggregation begins (the commencement of the plateau region) is a practical measure of the susceptibility of the soil to natural disruption and represents an absolute measure of the soils stability. The specific stability index for a brown earth soil with 4.4% organic matter and 46% clay was $25 \pm 3\ J_g^{-1}$.

2.6.8. Stability by Microaggregation Techniques

2.6.8.1. Suspension Density

This method entails flood wetting of air-dry aggregates

(1-2mm) and then subjecting them to between 5-20 minutes of end-over-end shaking (Quirk, 1950; Marshall, 1956; Carr and Greenland, 1972). After a suitable settling time the percentage of particles greater than 50μ and 20μ are determined with a plummet balance.

2.6.8.2. Turbimetry

Air-dry aggregates (1-2mm) are wet slowly to a suction of 30cm, placed in clear polystyrene tubes containing water and shaken end-over-end for a given period of time (Williams et al, 1966). The suspensions are allowed to stand until all particles of diameter greater than 2μ had settled to a level below which the light beam would pass. The percentage transmission is then determined using a turbidimeter. The ratio of a second reading, taken after a further period of time, to the first reading provides an index of water-stability of aggregates.

EXPERIMENTAL

3. MATERIALS AND METHODS

3.1. FACTORS AFFECTING SOIL AGGREGATE STABILITY IN SOILS COLLECTED FROM ENGLAND AND SCOTLAND.

3.1.1. Materials.

3.1.1.1. Soil Sampling

The majority of soils used in this study were collected in late summer. The exceptions were the soils of the Winton series which were sampled in early spring. The time of sampling of arable fields was restricted to the periods either before the cereal crop was sown or after it was harvested. The grassland soils from nearby fields were collected at the same time.

The method of sampling was to expose a soil profile with a spade and then take soil from various points between the soil surface and a depth of twenty centimetres using a trowel. Three samples were taken in close proximity and bulked to give a total soil weight of around five kilograms.

For the analysis to be carried out three size fractions were required; 2.0 - 2.8mm aggregates, less than 2mm and finely ground soil. Initially the soil was laid out to dry in the greenhouse and the 2.0 - 2.8mm soil aggregate obtained using sieves. The timing of this operation was important because if the soil was either too wet or too dry, great difficulty was experienced when sieving the soil. A representative sample of the soil passing through the 2mm sieve was also collected. Both these soil fractions were then air-dried at 50°C. The finely ground soil was obtained by splitting the less than 2mm soil with a sample splitter until five grams remained, and then grinding this in a mortar and pestel until it all passed through a 0.5mm sieve.

3.1.1.2. Soils sampled

Initially twenty-six soils were collected in Autumn, 1975. The eighteen soils from the East of Scotland (Appendix, Table A1) were sampled in August and September. A lateritic soil from Brazil has also been included for comparison. Table A2 of the Appendix shows the soils collected from England. The six soils from Lincolnshire and the soils from Rothamstead and Saxmundham were collected in October, 1975 and those from Essex and Warwickshire in September, 1977.

The soils collected from the Humbie series (12), the Kilmarnock series (10), the Stirling series (24) and the Winton series (22) are shown in the Appendix, Tables A3, A4, A5 and A6 respectively along with information concerning the farming practice.

The map of Britain shown in Figure 7 indicates the sampling sites of all the soils collected.

3.1.2. Methods.

3.1.2.1. Chemical and Physical Analyses

Carbon was determined by the wet-oxidation method of Tinsley (1950), but using as reagents 0.4N potassium dichromate, concentrated sulphuric acid, concentrated orthophosphoric acid, 0.4N ferrous ammonium sulphate and barium diphenylamine p-sulphonate indicator in barium chloride. Total nitrogen was determined by the semimicro-Kjeldahl procedure, using a titrimetric end (Black, 1965a).

Polysaccharide content was determined after hydrolysis by the phenol-concentrated sulphuric acid method (Dubois et al, 1956), using glucose as a standard. The optical density of the solution was measured at 480nm on a Unicam SP600 using 1cm cells. The hydrolysate for this method was obtained by hydrolysis with two strengths of sulphuric acid (Oades, 1967); end-over-end shaking with $24\underline{N}$ H_2SO_4 for 16 hours followed by refluxing for 5 hours with $1\underline{N}$ H_2SO_4.

Figure 7 Map of Great Britain showing the Distribution of the Soils Sampled

The humic acid content of soils were estimated by extracting finely ground soil with 0.1M sodium pyrophosphate (pH 7) and 0.5M sodium hydroxide. The 0.1M sodium pyrophosphate solution was a 1:1 mixture, with respect to molarity, of dihydrogen disodium pyrophosphate and tetra-sodium pyrophosphate. The solution was filtered to remove the small amount of dihydrogen disodium pyrophosphate which did not dissolve. A 25ml aliquot of 0.1M sodium pyrophosphate was added to 1g of soil in a 50ml polypropylene test-tube and shaken for 16 hours at 23°C. Fifteen minutes centrifugation at 7,000r.p.m. gave a supernatant whose optical density was measured at 400nm on the Unicam SP 600 using 1cm cells. After the supernatant had been decanted, 25ml of 0.5M sodium hydroxide were added and the procedure repeated. A second, separate extraction, omitting the pyrophosphate extraction, was carried out by adding 25ml of 0.5M sodium hydroxide to 1g of soil.

Cation exchange capacity was measured by three methods:-

(i) Leaching with ammonium acetate (pH 7). Soil ground to 2mm was leached with ammonium acetate (the leachate can be used for determining the exchangeable bases), and then with ethanol to remove the excess ammonium acetate. The soil was then leached again with 1N sodium chloride and the leachate distilled with magnesium oxide as described by Metson, (1956).

(ii) Barium-magnesium equilibrium (Bascombe, 1964). Finely ground soil (1g) was saturated with Ba^{2+} ions by shaking, centrifuging and decanting three 25ml aliquots of 0.1N barium chloride in triethanolamine buffer. After the third decantation 40ml of distilled water were added to remove any $BaCl_2$ from the system. After shaking, the soil was centrifuged to form a stable soil pad. The tube was weighed after decantation. A 25ml aliquot of 0.01N $MgSO_4$ was added and the tube shaken for 60 minutes to allow the system to equilibriate.

After a suitable dilution an aliquot was aspirated into an atomic absorption spectrophotometer and the Mg^{2+} concentration determined. By recording the dry weight of the soil pad, a correction in the calculation can be made for the amount of distilled water in the soil pad.

(iii) Equilibriating with Calcium -45 (Bache, 1970). Finely ground soil (0.5g) was saturated with Ca^{2+} ions by shaking, centrifuging and decanting three 40ml aliquots of 1M $CaCl_2$ solution. A 25ml aliquot of 2.5×10^{-3} M $CaCl_2$ (pH 7) was added, the test-tube shaken for 15 minutes, centrifuged at 7,000 r.p.m. for 10 minutes and then the supernatant decanted. This was repeated with a second 25ml aliquot and after decantation the weight of the tube plus the moist soil pad was recorded. A 25ml aliquot of 2.5×10^{-3} $CaCl_2$ (pH 7) labelled with Calcium-45 was added to each tube, and shaken for 2 hours. After centrifugation the number of counts/100 seconds were measured on a dried 1ml sample using a scintillation counter. The count rate of the original solution was also measured. Then the Cation Exchange Capacity =

$$\text{Cation Exchange Capacity} = \left(25 + \frac{\text{mls } CaCl_2}{\text{in soil pad}}\right) \times \frac{C \text{ total} - C \text{ soln}}{C \text{ soln}}$$

where C total = no. of counts/100 sec. for original solution

C soln. = no. of counts/100 sec. for supernatant solution

The total iron content of the soil was determined on an extract obtained by reducing 0.5g soil with 0.5g sodium dithonite and 10ml of citrate buffer. After a suitable dilution the iron (Fe^{2+}) concentration is determined by atomic absorption spectrophotometry.

Particle-size analysis was carried out by the standard pipette method (Black, 1965b). Hydrogen peroxide was used to destroy the organic matter, followed by the addition of sodium hexametaphosphate and high speed stirring to disperse the soil. The fractions collected

were coarse sand > ·2mm, fine sand ·2mm - ·05mm, silt ·05 - ·002mm, and clay > ·002mm; the U.S.D.A. classification.

Liquid limit was determined by both the cone penetrometer (British Standards Institution, 1975a) and the Cassegrande apparatus (British Standards Institution, 1975b). Plastic limit was determined as described in British Standards Institution (1975c).

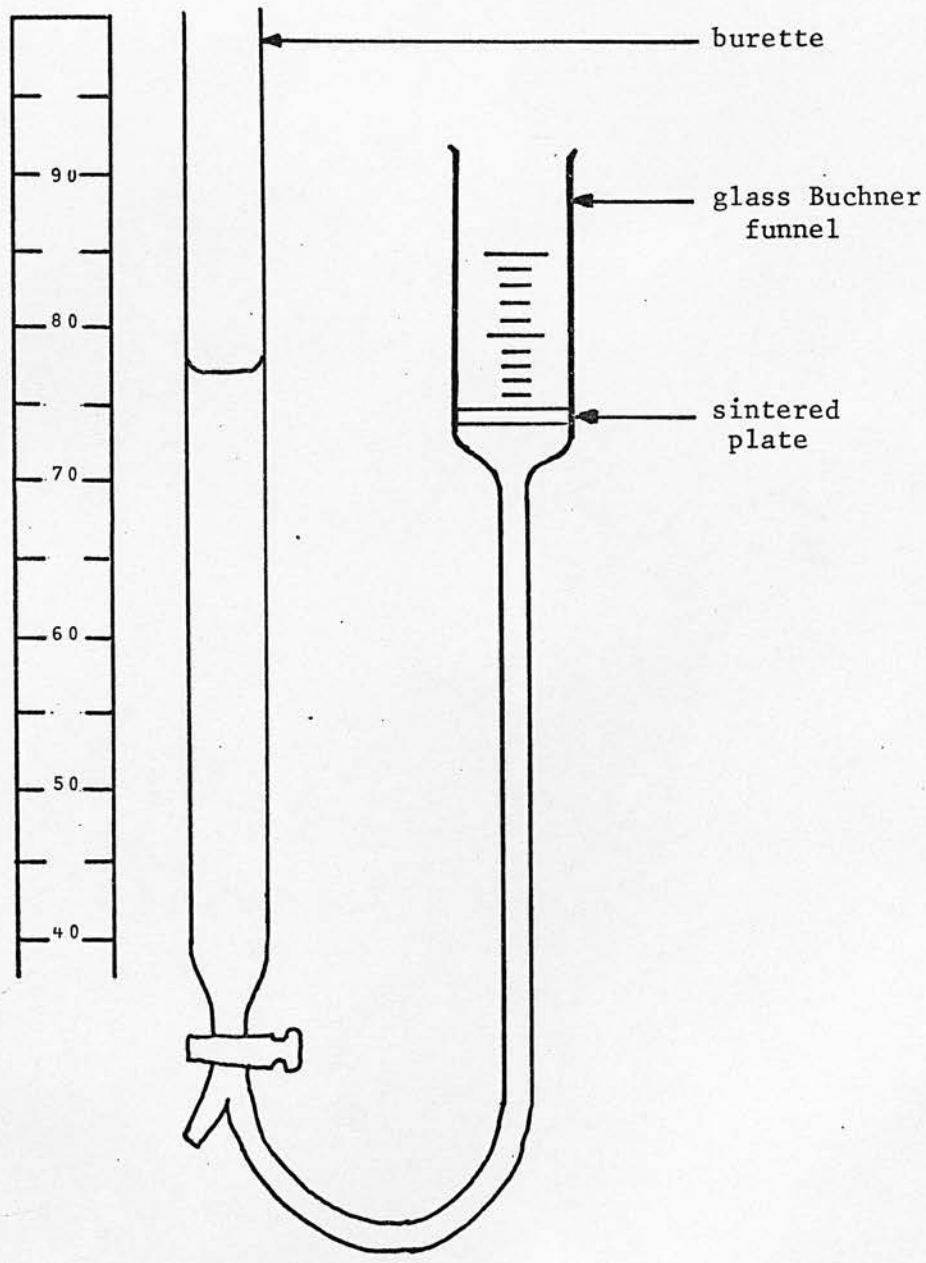
3.1.2.2. Methods for Evaluating the Stability of Soil Aggregates

(a) Aggregate stability by a modified moisture characteristic method. (Ingram, unpub.)

Three 15g samples of air-dried 2.0 - 2.8mm soil aggregates were weighed into 50ml beakers and placed in a humidity chamber (relative humidity 96-100%) at room temperature overnight. The following morning the crumbs in two of the beakers were slowly moistened, one was then left to dry out at room temperature. The other was placed in the deep-freeze at -15°C overnight, allowed to thaw the next day and dry out slowly at room temperature. Both sets of treated crumbs were then placed in a well-aerated oven maintained at 50°C to complete the drying process.

The air-dried soil aggregates, both treated and untreated were transferred from the beaker to the sintered funnel of the apparatus shown in Figure 8. The level of the funnel had been previously adjusted so that water just covered the sinter. As water was drawn up into the soil the burette was raised gradually until the aggregate bed was finally flooded to a depth of 1cm. The apparatus was left overnight. Next morning the burette was lowered until the surface aggregates were just above the water level in the funnel. With the tap off, the burette was nearly emptied and adjusted so that the water level in the burette was level with the top of the soil aggregate and the tap reopened. The total volume of the soil

Figure 8 Apparatus for Obtaining the Stability Index by a Modified Moisture Characteristic Method.



aggregates and water, V, in the funnel was recorded, along with the height of the mid-point of the aggregate bed from the bench top.

The burette was lowered 1-2cm and, when the meniscus has reached a new equilibrium position, its height above the bench top, H_1, and the burette reading, V_1, were recorded. A series of readings of H and V were obtained as the increasing tension withdrew water from the soil aggregates. When either a further large increase in tension failed to produce a change in volume, or the meniscus in the burette was below bench top level, the final readings of H and V were taken and the tap turned off. The soil in the funnel was then transferred to a weighed foil tray and weighed immediately, placed in the oven at 105°C overnight and reweighed. The loss in weight on drying was taken as being equal to the volume of water held by the aggregates against the final tension recorded.

The difference between the final burette reading and this volume was then subtracted from each of the recorded burette readings. The % volumes were then calculated by dividing these volumes by V, the total soil volume, and multiplying by 100. The difference between the height of the mid-point of the aggregate bed above the bench top and that of the mensicus in the burette gave the value of the actual tension applied at each reading, 'h' ($h_1 = H-H_1$; $h_2 = H-H_2$).

An index for aggregate stability can be calculated from the moisture characteristic curves by plotting the actual tension 'h' against the percentage volume. The index is the ratio of the percentage pores emptied between 0 and 10cm tension for treated crumbs to the percentage pores emptied between 0 and 10cm for untreated crumbs.

(b) Stability index by the water drop method. (McCalla, 1944)

The apparatus consisted of a 50ml burette clamped 20cm above

a 2.0mm grid wire gauze placed over a beaker. A 2.0 - 2.8mm air-dried soil aggregate was placed on the grid in such a position so that when the tap of the burette was opened water drops would fall directly onto the aggregate. The tap was then opened and the number of water drops hitting the aggregate were counted until the soil aggregate disintegrated sufficiently to be washed through the 2mm grid.

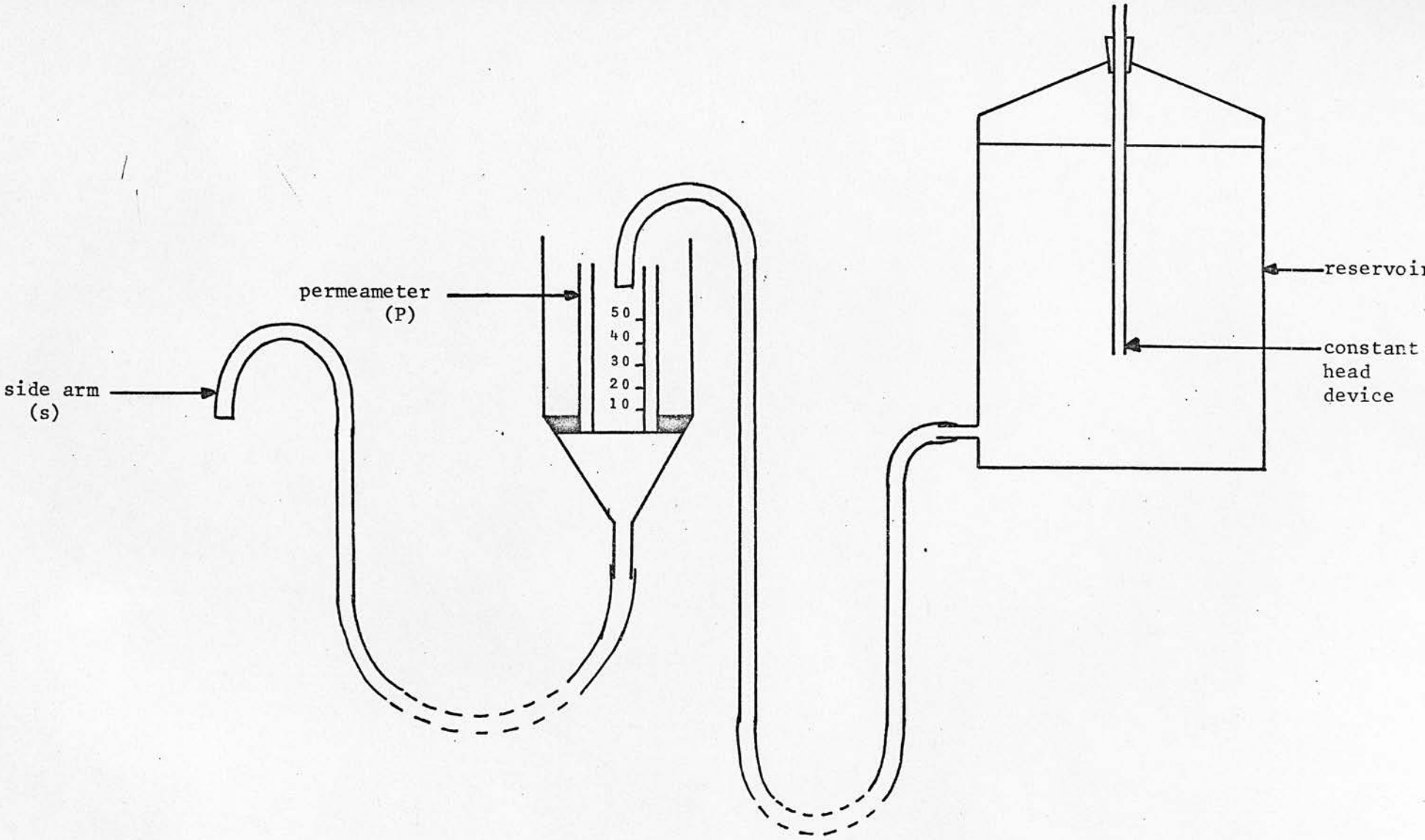
(c) Stability index by leaching with sodium chloride

Leaching with decreasing concentrations of sodium chloride. (Emerson, 1954)

The apparatus used was that shown in Figure 9 consisting of a 2 litre aspirator that was a reservoir for the electrolyte and a permeameter with a side-arm attached. However, in this experiment the permeameter was filled to a depth of 30mm with air-dried soil aggregates (2.0 - 2.8mm). The aggregates were wetted slowly with 0.5M sodium chloride by raising the side-arm, the first electrolyte to be used.

The constant head device in the reservoir was adjusted so that when the taps were open there was always a head of electrolyte in the permeameter. The initial permeability of the aggregates was measured immediately and subsequently at intervals of 15 minutes. Electrolyte was passed through the permeameter at a steady rate so that after 2 hours, 2 litres would have flowed through. The reservoir was then filled with 0.1M sodium chloride and the procedure repeated. Further decreases in the electrolyte concentration (0.05, 0.01, 0.005, 0.001, 0 M) were made until the permeability of the soil aggregates fell to zero, i.e. the aggregates have slumped or collapsed. The sodium chloride solution with which this occurred is termed the critical

Figure 9 Apparatus for Obtaining the Stability Index by Leaching with Sodium Chloride



concentration and is taken as the index of aggregate stability.

Leaching with a single concentration of sodium chloride. (Dettman and Emerson, 1959)

The apparatus (Figure 9) consisted of a permeameter (P) with a side-arm (S) and a 2 litre aspirator to give a constant head of electrolyte. The permeameter was a perspex cylinder, 30mm in diameter and 70mm long. It had a piece of nylon gauze attached at one end, with the zero mark of a scale from 0-50mm at this level. The aspirator was filled with 0.5M sodium chloride and the level of the constant head device adjusted to give a 40-50mm height of electrolyte in the permeameter. One millimetre diameter glass beads were added to the permeameter to give a 10mm thick layer free from air bubbles. With the reservoir disconnected the side limb was lowered until the electrolyte level was just below the glass beads. Air-dried soil aggregates (2.0-2.8mm) were placed on the glass beads to a depth of 10mm. As the aggregates became wet the side-arm was raised gradually until the level of electrolyte was 10cm above the soil. The side-arm was clamped in position so that the outlet was at the same level as the glass bead / soil aggregate interface.

When the reservoir tap was opened the rate of discharge of the electrolyte was measured - this was the initial permeability (K_1). Three litres of electrolyte were passed through the permeameter over a period of 24 hours. Then the rate of discharge was measured again, under the same conditions, to obtain a value for the final permeability (K_2). The final thickness of the soil aggregate bed was also noted at this time.

The permeability of the glass beads (K_s) was measured without soil aggregates in the permeameter. Due to their larger size and irregular shape, the 2.0 - 2.8mm soil aggregates will have a different

permeability to that of the spheroidal glass beads. By dividing the initial permeability of the 2.0 - 2.8mm soil aggregates (K_1) by the permeability of the glass beads alone (K_s), a factor was obtained which took account of these differences. The ratio $\frac{K_1}{K_s}$ had a value of 1.1, which was the same for any sample of 2.0 - 2.8mm soil aggregates.

The ratio of the final permeability (K_2) to the initial permeability (K_1) was then calculated from the equation:-

$$\frac{K_2}{K_1} = \frac{t_1 \; z_2}{t_2 z_1 \; (t_2 - t_1) \; z_s} \; K_1/K_s$$

where z_1 the initial soil aggregate bed thickness

z_2 the final soil aggregate bed thickness

z_s the glass bead bed thickness

t_1 the time for 100ml of electrolyte to flow initially

t_2 the time for 100ml of electrolyte to flow finally

(d) Slakings observations (Emerson, 1967)

Air-dried soil aggregates 2.0 - 3.5mm in diameter were placed in 20ml of distilled water in a beaker and observations made on their subsequent behaviour, with respect to swelling, slaking (disintegration) and dispersion. If the aggregates slaked the time for complete disintegration to take place was also recorded.

These observations were also made on individual air-dried aggregates wetted with water under vacuum and wetted with paraffin and ethanol.

(e) Wet-sieving

Standard method. Aggregate stability was measured using a modification of the wet-sieving method used by Tiulin (1928). The 2.0 - 2.8mm soil aggregates were prewet with an atomiser spray and the

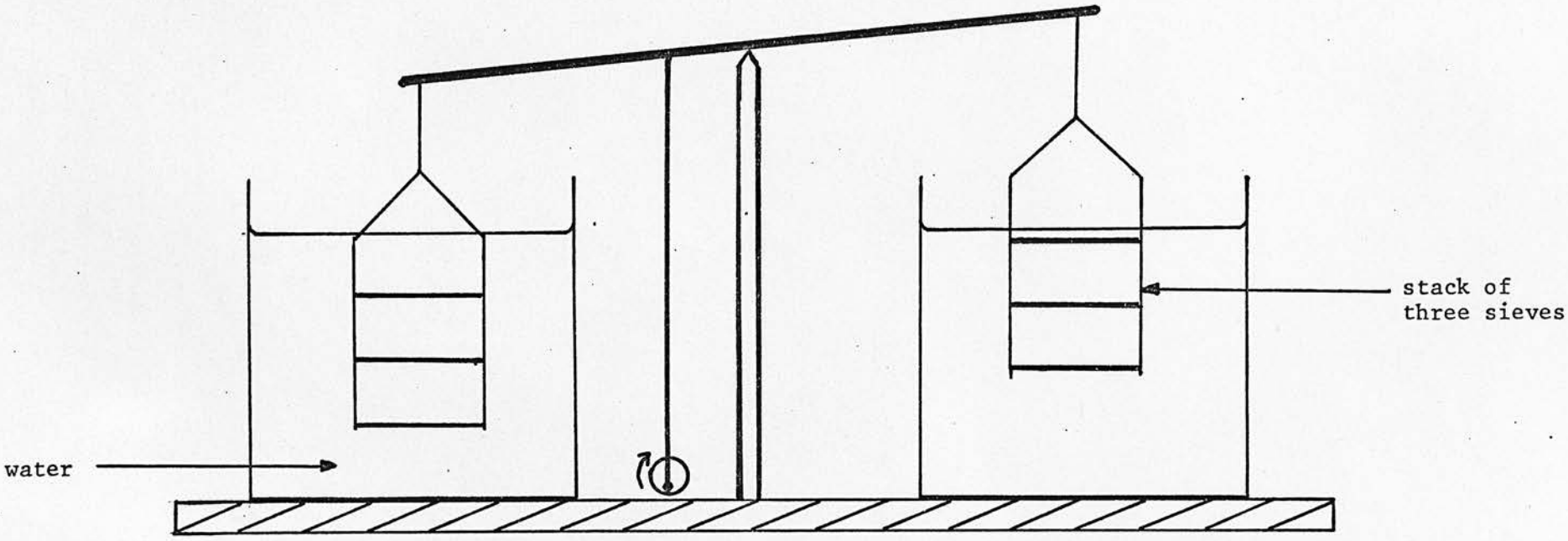
samples were then transferred to the uppermost of a stack of three sieves consisting of 2.0, 1.2 and 0.5mm sieves (Figure 10). The machine was operated for four minutes at a rate of 50 oscillations per minute. The soil remaining on each sieve was washed into a previously weighed foil tray and dried overnight at 105°C. The percentage of the total soil weight retained on each sieve plus that passing through the bottom sieve was then calculated. The mean weight diameter was obtained by multiplying the percentage of soil on the 2.0, 1.2, 0.5 and < 0.5mm sieves by 2.4, 1.6, 0.85 and 0.25 respectively (i.e. the mean intersieve values). The sum of these products is known as the Mean Weight Diameter, which, for the apparatus used here, has a maximum value of 240 and a minimum value of 25.

No pretreatment of soil aggregates. When the soils collected from the East of Scotland were wet-sieved initially, the air-dried aggregates were placed directly onto the 2.0mm sieve without any pretreatment. The wet-sieving procedure as described in the 'standard method' above was otherwise the same.

Mean weight diameter corrected for stone. A sample of air-dried soil aggregates was wet-sieved according to the 'standard method' described above, but after the foil trays were weighed, sodium hexametaphosphate was added to disperse the soil. The contents of each foil tray were placed on the relevant sieve, for example, the soil remaining on the 2.0mm sieve was placed on this sieve, and the dispersed soil washed through. Any particles of stone or gravel remaining on the sieve was transferred to a foil tray, dried at 105°C and weighed. The mean weight diameter was calculated using a figure for the initial weight of 2.0 - 2.8mm soil aggregates that was corrected for the amount of stone or gravel > 0.5mm. The weight of

Figure 10

The Wet-Sieving Apparatus



soil remaining on each sieve was also corrected for the amount of stone retained.

Moist soil aggregates. A sample of moist soil aggregates, 2.0 - 2.8mm, was also wet-sieved by the 'standard method'. No pretreatment was required.

3.2 LABORATORY STUDIES EXAMINING THE ROLES OF VARIOUS ORGANIC COLLOIDS ON THE FORMATION AND STABILISATION OF SOIL AGGREGATES.

3.2.1. Materials.

The six soils used in this section were chosen from the soils listed in Tables 1 and 2 of the Appendix. The date of sample collection was the same in both cases, but a sample of 15 - 20kg was taken to provide sufficient soil for the experiments carried out.

The permanent pasture (S_p), arable (S_a), and arable subsoil (S_s) of the Stirling soil series, obtained from Bridge of Earn, Perthshire, have been used most frequently in the incubation studies. The Stirling series is a poorly drained silty-clay loam from estuarine low raised beach silts and clays. Three sandy clay loam soils were also used in some experiments; these were Kilmarnock series (K_a), Ragdale series (R_a) and Beccles series (S_x).

All the soils used in this section were finely ground to < 0.5mm using a hammer mill with the appropriate grid.

3.2.2. Methods.

3.2.2.1. The Extraction of Humic and Fulvic Acids

Humic and fulvic acid were extracted from soils using first 0.1M sodium pyrophosphate at pH 7 followed by 0.5M sodium hydroxide. Five hundred gram samples of moist or dry soil were placed in 1 litre

polypropylene containers, which were then filled with 0.1M sodium pyrophosphate (1 : 1 ratio of disodium dihydrogen pyrophosphate and tetra sodium pyrophosphate) and sealed. The containers were then shaken end-over-end for 24 hours.

The liquid in the containers was then centrifuged at 3,000 r.p.m. for 20 minutes (4 X 360 ml). The supernatant containing the humic and fulvic acid was decanted into a beaker and the residue returned to the original containers. The supernatant was then recentrifuged at 7,000 r.p.m. for 15 minutes (6 X 100 ml), and the supernatant decanted into a beaker and the residue returned to the original containers. The pH of the supernatant solution was adjusted to pH 1-2 with 1M hydrochloric acid and then centrifuged at 7,000 r.p.m. for 10 minutes (6 X 100 ml). The supernatant of this centrifugation containing fulvic acid and polysaccharide material was decanted off and placed in dialysis tubing to remove pyrophosphate, chloride and other ions. The volume was reduced by rotary evaporation prior to freeze-drying the fulvic acid in the hydrogen ion form.

The residue (humic acid and small traces of inorganic material) was dissolved at pH 7 using distilled water and 1M sodium hydroxide. The solution was centrifuged again at 7,000 r.p.m. for 15 minutes (6 X 100 ml). The residue, if any, was returned to the original containers. The pH of the supernatant was adjusted to pH 1-2 with 1M hydrochloric acid and then recentrifuged at 7,000 r.p.m. for 10 minutes. The residue, humic acid in the hydrogen ion form, was dialysed and the slurry freeze-dried.

A further extraction was carried out on the same soil using the procedure described above but using 0.5M sodium hydroxide in

place of the pyrophosphate solution.

3.2.2.2. Dialysis

The tubing used for dialysis was 32/32 visking dialysis tubing membrane. This was boiled for 15 minutes in distilled water before use to remove deposits of glycerol. A length of tubing between 20 - 80 cm in length was filled with the solution or suspension to be dialysed, taking care to ensure that air was not present in the tubing. This was then placed in as large a volume of dionised water as practicable; the water was changed twice a day.

When chloride was present in the original sample, the completion of dialysis was monitored by testing for the presence or absence of chloride using silver nitrate. If chloride was not present an alternative test, such as measuring the sodium ion concentration with the flame photometer or monitoring the conductivity, could be employed.

3.2.2.3. Rotory Evaporation

Rotory evaporation can be a convenient means of reducing the volume of a solution. For example, in the extraction of humic and fulvic acid (Section 3.2.2.1.) a few litres of dilute fulvic acid solution was obtained. To freeze-dry this volume would be a lengthy process and therefore rotory evaporation was used to concentrate the solution.

The apparatus used was a Bucchi Rotorvapor - R together with a vacuum pump and a waterbath maintained at 60^{o}C.

3.2.2.4. Freeze-Drying

In a freeze-drier ice is sublimed from the sample, in a flask attached externally, and condensed at the coldest part of the system - a refrigerated unit maintained at -40^{o}C. For the process to

take place efficiently it is necessary for the system to be evacuated to pressures of 10^{-1} torr or less. If salts are present in the sample the energy required for the ice to sublime is much greater than for a salt-free sample and the sample melts. For this reason all samples were dialysed prior to freeze-drying.

Approximately 250 ml of the sample were transferred from the dialysis tubing to a 1 litre quickfit flask. This was then frozen down by rotating the flask in a freezing mixture (liquid nitrogen, liquid air or dry ice and ethanol) ensuring that as large a surface area as possible of the flask was covered. The flask was then attached to one of the outlets of the freeze-drier.

The freeze-drier was a 2 litre capacity SB3 model (Chemlab Instruments, Ilford, Essex). It was fitted with a Pirani gauge and head, and an Edwards ED50 vacuum pump. The manifold was T-shaped with four outlets, each of which had an isolation valve.

3.2.2.5. Fractionation of Humic Acid

Humic acid was fractionated with respect to molecular weight using an Amicon Ultrafiltration Cell (Model 202). Humic acid in the hydrogen ion form was slurried in 400 ml of distilled water and adjusted to pH 7 by adding 1M sodium hydroxide. The humic acid solution (now sodium saturated) was transferred into an Amicon cell fitted with an ultrafiltration membrane that allows molecules with molecular weights of less than 300,000 to pass through. The Amicon cell was then connected to a nitrogen cylinder and sufficient pressure applied (~ 20 - 25 lb/sq in) to give a reasonable flow rate through the membrane. When the volume of solution in the cell had been reduced to one third of the capacity, the cell was opened and the > 300,000 fraction removed.

To ensure that all the molecules less than 300,000 had passed through the membrane, more distilled water was added to the > 300,000 fraction and the procedure repeated. The fraction less than 300,000 was then fractionated again with an ultrafiltration membrane partitioning at a lower molecular weight value (50,000). Finally the humic acid fractions were freeze-dried.

3.2.2.6. Preparation of Ca^{2+} or Na^{+} Saturated Soil

To prepare calcium-saturated soil approximately 500 ml of distilled water was added to 500 g of soil in a 2 litre plastic beaker, mounted on a magnetic stirrer. Five hundred millilitres of 2M calcium chloride solution were added and this was stirred continuously for 2 hours. When the soil had settled the supernatant was decanted off and more distilled water added. After a second decantation, the soil was transferred to dialysis tubing (32/32) to remove the remaining salts before freeze-drying.

When preparing sodium-saturated soil, 2M sodium chloride was used, and only one decantation was carried out after stirring. If a second aliquot of distilled water was added, the soil tended to disperse, giving a large volume to be freeze-dried.

3.2.2.7. Preliminary Adsorption Experiments

Two grams of humic acid (in the hydrogen ion form) were slurried in 600 ml of distilled water and dissolved by adding 1M sodium hydroxide until the pH was stable at 7; the final volume was adjusted to one litre. Fifty millilitres of this solution were added to 5 g of sodium saturated Stirling subsoil (Sa Na^{+}) in a 100 ml polypropylene test-tube. The pH of the resulting mixture was adjusted to 3.5 by adding 1M hydrochloric acid dropwise using a small magnetic stirrer in the bottom of the test-tube to attain equilibrium faster.

With each set of test-tubes two controls were set up; one had 5g of soil with humic acid solution at pH 7, and the other had humic acid solution adjusted to pH 3.5 only. After shaking all the test-tubes for 2 hours on an end-over-end shaker they were centrifuged at 7,000 r.p.m. for 15 minutes. The optical density of the supernatant solution was measured on the Unicam S.P. 600 using 1cm cells and compared with that of the original humic acid solution. The optical density of the original humic acid solution was also recorded.

Similar experiments were conducted using sodium- and calcium- saturated Stirling subsoil, natural Stirling subsoil, sodium- and calcium- saturated Stirling arable, natural Stirling arable, natural Kilmarnock arable and natural Ragdale arable.

3.2.2.8. Preparation of Reformed Soil Aggregates

The aggregate stability of all reformed aggregates was assessed on 2.0 - 2.8mm air-dried aggregates in all the following experiments.

(a) Artificial aggregates formed by cutting

Approximately 200g of soil was moistened to a 'sticky state' and then smoothed out to a depth of 3 - 5mm. Using a scalpel, this soil paste was then cut into small cubes, which were then left to dry out completely at 50°C.

(b) Wetting and drying cycles

Approximately 200g of soil was moistened to 20cm tension on a tension tank and then dried at 30°C. This procedure was repeated 5 times, 10 times and 15 times.

(c) Freezing and thawing cycles

Approximately 200g of soil was moistened to a 'sticky state' and placed in the deep-freeze at -15°C in a sealed plastic bag overnight. The soil was then transferred to a foil tray and placed in an

incubator maintained at 30°C until it was dry (2 days). This cycle was repeated 5 times, 10 times and 15 times.

(d) Wetting and drying plus freezing and thawing

The procedure employed was a combination of both methods (b) and (c) above.

3.2.2.9. Reformation of Aggregates using Additions of Organic Materials

(a) Additions of synthetic organic materials

Additions of glucose, starch etc. were made at the 5% level to 200g of soil in an aluminium foil tray and mixed in thoroughly. Also at this time a small amount of finely ground, air-dried soil from the Stirling permanent pasture (S_p) was added to each sample to ensure a complete range of microorganisms. Distilled water was added with stirring until the soil was moist throughout. The sample was then placed in an incubator maintained at 30°C for 3 weeks. The soil had to be remoistened every second day throughout the incubation period.

(b) Incubation with a specific soil microorganism

Twenty millilitres of 10% glucose solution inoculated with azotobacter, a soil microorganism which produces alginate, were added to 100g of soil from Ragdale arable (R_a), Stirling arable (S_a) and Stirling subsoil (S_s), in a 2 litre wide-mouthed conical flask. Distilled water was added with stirring until the soil was moist throughout. The flask was covered with tin foil and placed in the incubator at 30°C for 2 weeks. A control flask was prepared for each soil without the azotobacter innoculum.

(c) Incubation experiments using a 0.5% addition of glucose

Long term experiment. A 1.25g addition of glucose was made to 250g of soil (S_s or S_a) in an evaporating dish (diameter 145mm) and mixed in thoroughly. A small amount of finely ground soil from Stirling permanent

pasture containing a complete range of microorganisms was added to each sample. Distilled water was added with stirring until the soil was moist throughout. The dish was then covered with tin foil and placed in an incubator at 30°C. A sample of 2.0 - 2.8mm soil aggregates were removed and wet-sieved after 1, 3, 5, 8 and 12 weeks.

Reproducibility experiment. Seven basins with 200g of Stirling subsoil and three basins with 200g of Stirling arable and 0.5% glucose were set up as described above. A control for each soil was also set up omitting the glucose. These samples were incubated for 3 weeks, sampling the 2.0 - 2.8mm aggregates for wet-sieving at intervals of seven days.

Incubation with a wetting and drying cycle. Three 200g samples with 0.5% glucose and three controls of Stirling permanent pasture (S_p), arable (S_a) and subsoil (S_s) were set up as described above. After one week the tin foil was removed and the sample dried out completely at 50°C. The sample was remoistened as before with distilled water and the incubation continued for another week. The 2.0 - 2.8mm soil aggregates were removed and wet-sieved.

Incubation with a split addition of glucose. This experiment was the same as the incubation with a wetting and drying cycle except a 0.25% addition of glucose made initially and a second 0.25% was added when the soil was remoistened.

(d) Reformation of aggregates by addition of synthetic and natural polysaccharides

Experiment to find the amount of polysaccharide necessary to form stable soil aggregates. The polysaccharides - Xanthan gum and Azotobacter alginate - were added at the 0, 0.05, 0.075, 0.1, 0.25 and 0.5 per cent level to 100g samples of Ragdale arable (R_a), Stirling arable (S_a), Stirling subsoil (S_s) and Beccles arable (S_x).

The polysaccharide was dissolved in 50ml of distilled water before addition to the soil and then mixed in to form a paste. This was dried at 50°C. As the soil dried it was broken up by hand until finally 2.0 - 2.8mm soil aggregates were sieved out and used for wet-sieving.

Addition of polysaccharides to natural soil aggregates. A polysaccharide solution in the sodium form (pH 7) containing 0.1g of Xanthan gum or Azotobacter alginate in 50ml of distilled water was added to 50g samples of natural soil aggregates. The solution was sprayed onto the aggregates using an atomiser; if the aggregates became damp then the spraying was continued. When all the solution had been added the soil aggregates were dried out completely and wet-sieved.

(e) Incubation experiments in which the production of carbon dioxide was monitored

The additive and soil were placed in a 500ml quickfit flask and mixed thoroughly. A small amount of finely ground, air-dried soil of Stirling permanent pasture (S_p) was added to each sample to provide a complete range of microorganisms. The soil was moistened to a 'sticky state' with distilled water and the flask sealed with a suba-seal before being placed in an incubator maintained at 30°C. One millilitre gas samples were taken at regular intervals and analysed using a gas chromatograph. When the level of carbon dioxide in the flasks rose above 2% the suba-seal was removed, the flask flushed with air and the suba-seal replaced.

(f) Reformation of aggregates by physical addition of humic and fulvic acids

Humic and fulvic acids in the sodium and calcium forms (at pH 7) were added at the 2% level to various samples of finely ground

soil in evaporating basins. Soil of Stirling arable, Stirling subsoil and Kilmarnock arable together with sodium- and calcium- saturated soil of all three were used in the experiments. A 0.5% glucose addition or a 0.2% polysaccharide addition was made to some samples to provide an energy source for the microorganisms. A small amount of Stirling permanent pasture soil was added to each soil to ensure a complete range of microorganisms was present. Distilled water was then added until the soil was moist throughout. The dishes were covered with tin foil and placed in the incubator for 2 weeks.

3.2.2.10. Incubation Experiments to Reform Soil Aggregates by the Adsorption of Organic Compounds

Humic or fulvic acid in the hydrogen ion form was weighed out accurately and slurried in approximately 400ml of distilled water. Sodium hydroxide (1M) was added dropwise as the slurry was stirred continuously with a magnetic stirrer until the pH was stable at 7. The solution was stirred for several hours to ensure the humic acid was completely dissolved, before being added to the finely ground soil in a 2 litre beaker and the volume adjusted to 1 litre with distilled water. The pH was adjusted with 1M hydrochloric acid, added dropwise, to pH 3.5 and stirred continuously with a magnetic stirrer for 2 hours.

The adsorption was terminated by the addition of 200ml of 1M calcium chloride solution and then a saturated calcium hydroxide solution was added until the pH was 7. When the fine particles had settled the supernatant was decanted and washed by repeatedly adding distilled water and decanting. To avoid redispersion the remaining salts were removed by dialysis prior to the sample being freeze-dried.

After freeze-drying the sample was incubated with a 0.5% addition of glucose in an evaporating basin. A small amount of

Stirling permanent pasture soil was added to each soil to ensure a complete range of microorganisms was present. Distilled water was then added until the soil was moist throughout. The dishes were covered with tin foil and placed in the incubator at 30°C.

4. RESULTS AND DISCUSSION

4.1. FACTORS AFFECTING SOIL AGGREGATE STABILITY IN SOILS COLLECTED FROM ENGLAND AND SCOTLAND

4.1.1. Preliminary Experiments to Find a Method for Determining Aggregate Stability

4.1.1.1. Introduction

Initially pairs of soils of the same soil series were collected from adjacent fields under continuous cultivation and permanent pasture, or from situations approximating as close to this as possible, at various sites in the East of Scotland and Lincolnshire (Appendix, Tables A1 and A2 respectively). The differences between the arable and permanent pasture soils of the Biel and Stirling soil series are illustrated in Plates I and II respectively. The striking feature of these photographs is the size of the clods that were sampled from the arable fields. For instance, the large clod from Stirling arable was over thirty centimetres in diameter. A comparison of these soils with the respective permanent pasture soils, which contain crumb or granular aggregates up to one centimetre in diameter, illustrates the effect that permanent grassland can have on improving soil structure.

A large proportion of the soils chosen were in the medium to heavy textural range, and many of the arable soils collected had known structural problems, such as compaction or capping, under the farming practice they sustained. By comparing these with the same soils under permanent pasture, in which the structural problems were less pronounced or absent, it was thought that the factors affecting aggregate stability would become evident during this study. Also by choosing to examine

Plate I Soil of the Biel Series Sampled from Continuous Cultivation and Permanent Pasture

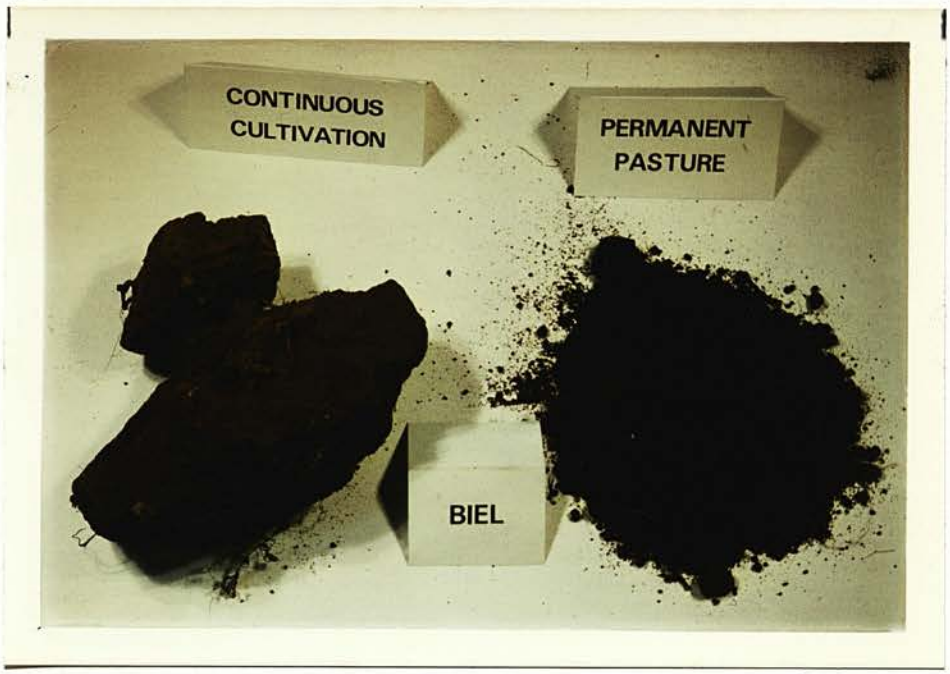
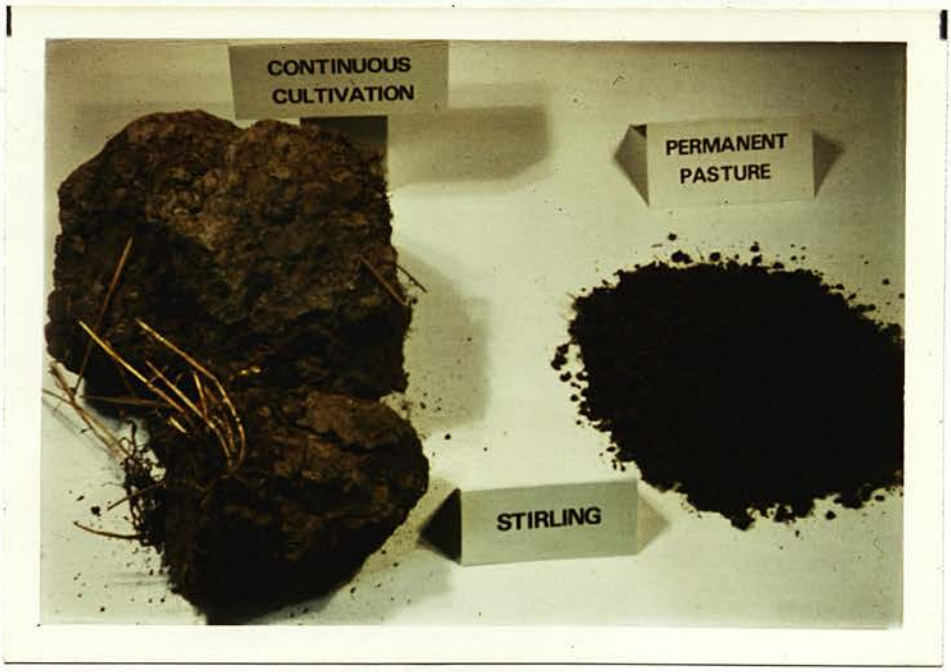


Plate II Soil of the Stirling Series Sampled from Continuous Cultivation and Permanent Pasture



heavier textured soils instability problems associated with many of the soils that contain a large proportion of sand particles would be avoided. In this way it may be possible to determine other factors which could be important in the formation and stabilisation of soil aggregates.

4.1.1.2. Aggregate Stability by a Modified Moisture Characteristic Method. (Ingram).

Treated and untreated soil aggregates from Humbie permanent pasture and arable and Kilmarnock permanent pasture and arable (Kilduff and Athelstaneford) were used for the modified moisture characteristic method. The percentage moisture held at 0cm and 10cm tension for untreated and treated soil aggregates for these five soils are shown in Table 2(a). The ratio of the percentage pores emptied between 0 and 10cm tension for treated and untreated soil aggregates did not give an indication of whether a soil was unstable or not.

This is consistent with the work of Rycroft and Thorburn (1974) who considered that, "The use of moisture characteristic curves in assessing water stability of clay soils thus remains qualitative". They came to this conclusion after examining quantitative indices based upon, a) the ratios between the maximum slopes of the slowly and rapidly wetted moisture characeristics, b) the areas bounded by the curves of slowly and rapidly wetted soils, c) the behaviour of rapidly wetted soils alone.

The ratios between the maximum slopes of the untreated and treated moisture characteristics of the Humbie and Kilmarnock soils were also calculated and are shown in Table 2(b). This appears to give an index with stable soils having a value less than 1, and more

Table 2(a) Results for the amount of water held a 0 and 10cm suction for the method of Ingram

SOIL	% moisture held at 0cm			% moisture held at 10cm		
	Untreated	Treated wet/dried	-15°C	Untreated	Treated wet/dried	-15°C
Ha	62	66	68	25	26	30
Hp	72	82	95	31	38	51
KKa	65	72	64	28	25	26
Kp	77	71	91	36	32	49
Ka	68	72	76	33	31	36
PFa	69	71	75	36	38	42

(b) Results for the ratio between the maximum slopes of the untreated and the treated moisture characteristics

Soil	Ratio
Ha	2.14
Hp	0.89
KKa	1.15
Kp	0.94
Ka	1.76

unstable soils having a value between 1 and 3.

However, no confidence could be placed in this method alone to give an index of aggregate stability. Its main value is for revealing important information concerning the pore-size distribution of soil aggregates.

4.1.1.3. Stability Index by the Water Drop Method. (McCalla, 1944)

This method has been used successfully by several investigators (e.g. Low, 1954; Griffiths and Jones, 1965), but in most cases electronic counting equipment was used to reduce the tedium of counting water drops for long periods. With the apparatus used in this study, poorly structured soil aggregates took between 100-500 water drops to disintegrate. The well structured soil aggregates from permanent pasture did not disintegrate even after being exposed to the drops for long periods of time.

As a method was required that would evaluate soil aggregate stability over a whole range of soils, the water drop method was not suitable for the studies to be carried out. This method would appear to be the appropriate one for measuring the stability of inherently unstable soils (e.g. subsoils), where the small differences in aggregate stability would be shown up. Also it can be used for determining the stability of small samples. However, the problem of whether a single aggregate is representative of a whole sample then arises.

4.1.1.4. Stability Index by Leaching with Sodium Chloride

Permeability methods depend on a chemical treatment to disrupt certain bonding forces within the soil aggregates. Having broken these bonds the aggregates swell and disperse to varying degrees depending on the effectiveness of the treatment. Therefore,

this method is giving a measure of the bonding forces within aggregates, whereas the wet-sieving method depends on unquantifiable mechanical disruption forces due to differential swelling, release of entrapped air after flood wetting, and the shattering and abrasive action of one particle on another.

Leaching with decreasing concentrations of sodium chloride (Emerson, 1954) The plot of flow rate of electrolyte against time (Figure 11) shows that the method easily distinguishes between a well structured permanent pasture soil (K_p) and the less stable aggregates of two arable soils (PF_a and KK_a). However, aggregates from the permanent pasture did not disperse using very low concentrations of sodium chloride or even when distilled water was used. This means that soils with high structural stability cannot be distinguished by this method. Also, comparing the results obtained for the Peffer and Kilmarnock arable soils, it can be seen that although the two curves are completely different, the concentration of sodium chloride at which the soils dispersed was the same.

This method is only applicable to soils with sufficient clay content. If it were absent, even if dispersion of the soil aggregates occurred, the geometry of the sand particles would allow some flow of electrolyte.

Leaching with a single concentration of sodium chloride (Dettman and Emerson, 1959) The ratio of the initial permeability to the final permeability of soil aggregates, after leaching with 0.5M sodium chloride, gives an index for aggregate stability which ranges from 0 to 1 (Table 3). Although the method distinguishes between the stable and unstable soils, it has difficulty in differentiating between soils with similar stabilities (e.g. PF_a and B_{nb}, or B_{hr} and S_p).

Figure 11 Plot of Flow Rate against Time for KKa, Kp and PFa

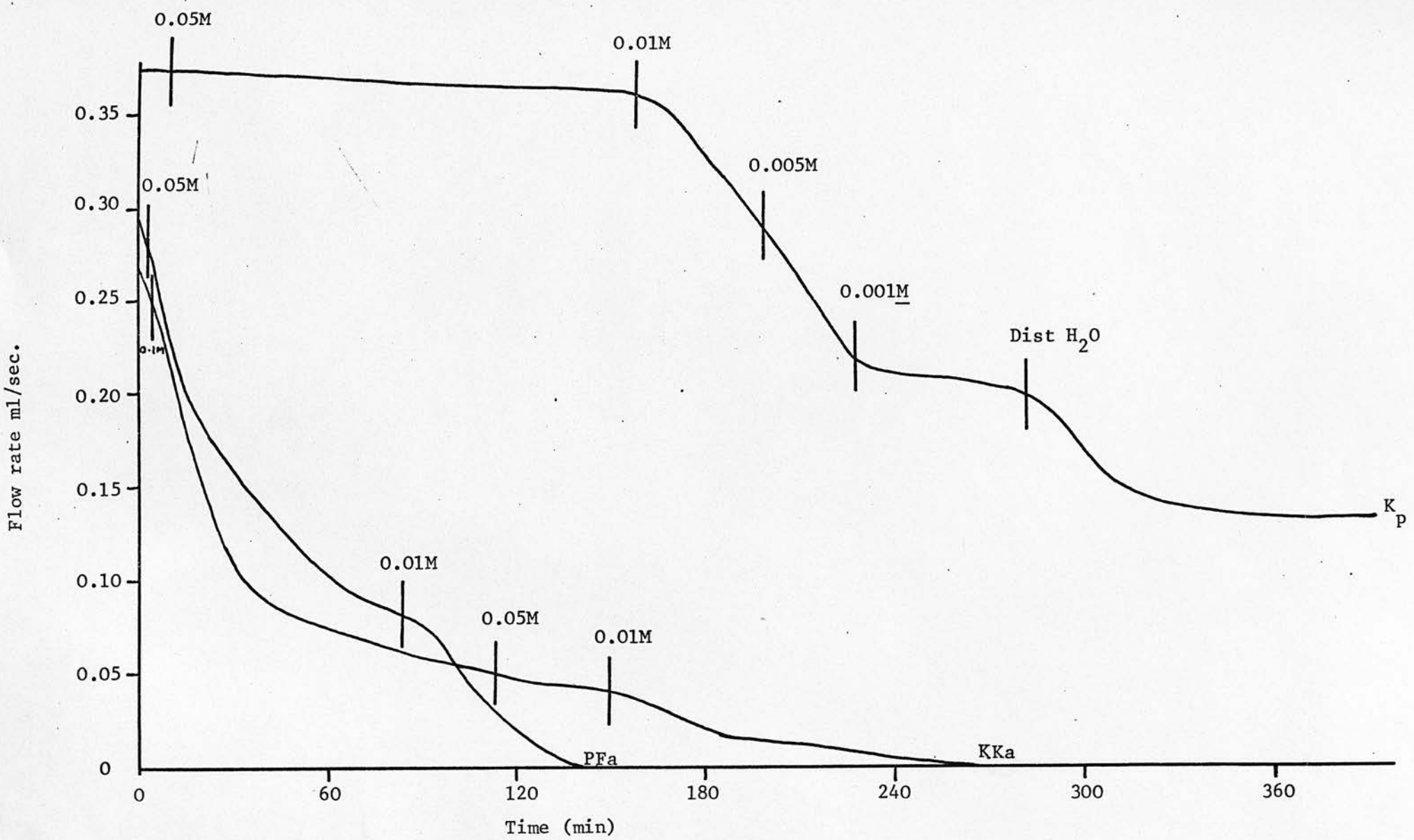


Table 3 Results for the stability index obtained by leaching with a single concentration of sodium chloride

SOIL	Initial flow rate t1	Final flow rate t2	Initial bed height Z_1 (mm)	Final bed height Z_2 (mm)	Stability Index
Ha	23	35	12	12	0.50
Hp	20	21	10	10	0.95
KKa	20	28	10	10	0.55
Kp	20	22	10	10	0.90
Ka	20	31	10	10	0.48
DRa	29	72	12	12	0.26
PFa	19	266	11	13	0.04
Bg	20	22	12	12	0.84
Ba	25	45	11	11	0.38
Bhr	20	20	12	12	1.00
Bnb	40	755	12	12	0.04
Sa	24	37	10	10	0.47
Sp	19	19	12	12	1.00
Pa	21	400	12	12	0.03
Phr	19	21	10	10	0.82

$$\text{Stability Index} = \frac{t_1 \cdot Z_2}{t_2 Z_1 + (t_2 - t_1).Z_s \; K_{1/K_s}}$$

where Zs = 10mm

$K_{1/K_s} = 1.1$

The main disadvantage of this method was the problem of obtaining reproducible results, the error on repeat determinations could be as high as 10%. Despite these problems the correlation coefficient for the index of aggregate stability and organic matter content for the samples studied has a value of 0.727; this is significant at the 1% level.

4.1.1.5. Slaking Observations

A soil aggregate is classified as having slaked when it has disintegrated into its separate constituents particles and could no longer be recognised as the original structured aggregate. If air-dried soil aggregates are placed straight into water disruption can occur due to (a) forces exerted by air entrapped within the aggregates, (b) differential swelling of soil aggregates containing clay, and (c) the energy of hydration on wetting.

The observations made on the behaviour of air-dried soil aggregates, 2.0 to 3.5mm, when rapidly immersed in water at atmospheric pressure are given in Table 4, along with the time the aggregates took to slake and the behaviour of the aggregates that slaked when wetted under vacuum. Of the twenty-six samples tested initially, aggregates from twelve soils slaked, and these were all from arable fields. When the aggregates were immersed, a succession of small bubbles was seen escaping from the aggregates. The first indication that slaking was occurring, was swelling of the aggregate, this was usually followed by cracks appearing, then the eventual disintegration of the aggregate. In some soils the process was very rapid taking 0-20 seconds (e.g. PF_a, F_a and F_f), in others slaking took a lot longer, 2-5 minutes in the case of B_a, S_a and P_a.

When a separate sample of aggregates, which had slaked at

Table 4 Observations on the behaviour of soil aggregates when rapidly immersed in water at atmospheric pressure and under vacuum

SOIL	Do aggregates slake at atmospheric pressure	Time	Do aggregates slake under vacuum	Did aggitation have an effect
Ha	NO			
Hp	NO			
KKa	SOME	2-5 min		
Kp	NO			
Ka	NO			
DRa	SOME	2-5 min		
PFa	YES	0-20 sec	NO	NO
Bg	NO			
Ba	YES	2-5 min		
Bhr	NO			
Bnb	NO			
Sa	YES	2-5 min	NO	NO
Ss	YES	0-60 sec		
Sp	NO			
Pa	YES	0-60 sec		
Phr	NO			
Fa	YES	0-20 sec	NO	NO
Fp	NO			
Ra	YES	0-60 sec	NO	NO
Rpl	NO			
Rip	NO			
Da	YES	5-10 min	NO	NO
Dp	NO			
Sx	YES	0-60 sec	NO	SLAKED
Bf	YES	0-20 sec	NO	SLAKED
Lt	NO			

atmospheric pressure, were wetted slowly with water under vacuum, no slaking occurred. Subsequent gentle agitation of the aggregates caused disintegration in two cases (S_x and B_f) out of the six soils tested. This indicates that although wetting is not causing slaking to occur, the process of hydration in these two soils has seriously weakened the structure of the soil aggregates. However, the fact that soil aggregates from four soils did not slake with gentle agitation suggests that there is another process weakening the structure. Since these aggregates did not slake under vacuum, it appears that air escaping from the aggregates is playing an important role in disintegration. Additional information was obtained when the aggregates were immersed in non-polar organic solvents, such as ethanol and paraffin. None of the aggregates slaked, but in all cases air could be seen escaping from the aggregates.

The observation that the aggregates did not slake when hydrated in non-polar organic solvents but did disintegrate when wet in water (a polar solvent), suggests that the process of water hydration is of extreme importance in relation to slaking of soil aggregates. One hypothesis is that hydration by a polar solvent such as water (together with swelling if it occurs) weakens the structure of the aggregates, and that the pressure exerted by entrapped air escaping from the aggregates provides the small amount of energy required for sub-aggregates or mineral particles to break away from the severely weakened aggregate.

In section 4.1.1.6. it is noted that in general where there was a large discrepancy in mean weight diameter between the MWD of soil aggregates with no pretreatment and those prewetted with an atomiser, slaking was observed to take place. Measurement of the heat of hydration using a microcalorimeter could provide important

information relating to slaking of soil aggregates, and possibly an index of aggregate stability as well.

Slaking tests as carried out according to Emerson (1967) and Greenland et al (1975) give observations distinguishing soils likely to suffer from structural problems in the field e.g. capping, poaching. However, for the work to be carried out in this study, it was desirable to use a method giving a single figure index of aggregate stability and therefore, slaking tests were of limited value.

4.1.1.6. Wet-Sieving Methods

The four wet-sieving methods described in section 3.1.2.2.(e) were used to obtain an index for aggregate stability and the results are presented in Table 5. The mean weight diameter (M.W.D.) is a single figure calculated from the distribution of the aggregates between the sieves, that can be used as an index of aggregate stability. Under the experimental conditions used it has a minimum value of 25 and a maximum value of 240. All four wet-sieving methods gave reproducible results with a wide range of mean weight diameter values (30 - 230), and readily distinguished differences between all the soils tested. A second aggregate stability index was calculated, the geometric mean diameter, which gave a range of values between 1.8 and 6.2, but this did not readily distinguish between all the soils.

The value for the M.W.D. was higher in all cases when the aggregates were prewet with an atomiser spray (Table 5, column 2) rather than being placed directly onto the sieve and flood-wetted (Table 5, column 1). An explanation for this fact could be that when the soil aggregates were immersed rapidly the incidence of soil aggregates slaking was much greater than when the aggregates were

Table 5 Mean weight diameter of air-dried aggregates with no pretreatment, prewetted with atomiser, prewetted with atomiser and corrected for stone, and moist aggregates

SOIL	1 no pretreatment	2 prewetted with atomiser	3 prewetted and corrected for stone	4 moist aggregates
Ha	111	132	119	131
Hp	193	225	224	220
KKa	84	98	82	162
Kp	211	219	219	217
Ka	129	148	141	198
DRa	45	71	58	116
PFa	34	53	51	113
Bg	208	215	205	222
Ba	42	82	75	91
Bhr	205	211	206	208
Bnb	54	72	47	149
Sa	41	118	116	116
Ss	28	37	36	75
Sp	218	223	222	221
Pa	31	54	50	146
Phr	204	215	211	212

The correlation coefficients for mean weight diameter and organic matter content for the four wet-sieving methods are :-

no pretreatment	r = 0.857
prewetted with atomiser	r = 0.848
prewetted and corrected for stone	r = 0.834
moist, fresh aggregates	r = 0.840

wet more slowly with a fine spray of water. Evidence supporting this view was obtained from the behaviour of air-dried soil aggregates when they were immersed in water (Table 4). When comparing the values for M.W.D. of aggregates with no pretreatment and those prewetted with an atomiser, it was noticed that where there was a large difference in M.W.D. slaking was observed to take place, e.g. DR_a, B_a, S_a and P_a. The reasons why soil aggregates slake were discussed in section 4.1.1.5.

The M.W.D. of the standard wet-sieving procedure was recalculated, correcting the amount of soil remaining on each sieve for the weight of stone and gravel greater than 0.5mm. For many soils the M.W.D. values were very similar in both calculations, but the value corrected for stone was lower for each soil than that of the standard method. The soils which did have a large discrepancy between the results had considerable amounts of sand present; for example, the particle size analysis of B_{nb} showed it contained 57% sand.

Mean weight diameter values for the fresh, moist soil aggregates (Table 5, column 4) were always greater than those for aggregates wet-sieved with no pretreatment. The values for fresh, moist soil aggregates was two times or more greater than that with no pretreatment in the case of poorly structured arable soils. The results for aggregates from permanent pasture soils, prewet with an atomiser, were similar to those of fresh, moist aggregates, but the fresh, moist aggregates from arable soils tend to have a much higher M.W.D. than those of dried then prewetted aggregates.

Expressing this another way the air-dried soil aggregates have a much larger range of mean weight diameter values than moist

aggregates. A similar result was obtained by Low (1954). He found that soils which were known from field observations to be quite different in physical behaviour could give very similar results when wet-sieved in a fresh, moist state. Values more closely related to field observations and performance were obtained when aggregates were wet-sieved after air-drying.

The correlation coefficients (r) of the mean weight diameter and organic matter content for the four methods of wet-sieving are given in Table 5. In each case the correlation coefficient is significant at the 0.1% level; i.e. the stability of aggregates increases with increasing organic matter levels, which is the expected result from the behaviour of soils in the field. Although the gradients of the regression lines for the graphs of M.W.D. and organic matter were similar in the four methods, the intercept of the y-axis (% organic matter = 0) was nearest to the minimum mean weight diameter figure of 25 when the aggregates were prewetted with the atomiser. Plots of organic matter against mean weight diameter are shown in Figure 12 for the four wet-sieving methods.

After these preliminary experiments it was decided to use air-dried soil aggregates and an initial prewetting with an atomiser spray for wet-sieving measurements. Although the stability of fresh, moist soil aggregates from arable soils was higher than that of air-dried aggregates, the latter were desirable because air-drying eliminates variables such as the moisture content in the initial sample. Also, gentle wetting of the air-dried soil aggregates prior to wet-sieving, with an atomiser spray, reduced the amount of slaking that occurred when the aggregates were immersed on the sieves.

Figure 12 Plots of Organic Matter Content against Aggregate Stability (MWD) for the Methods used in the Preliminary Study

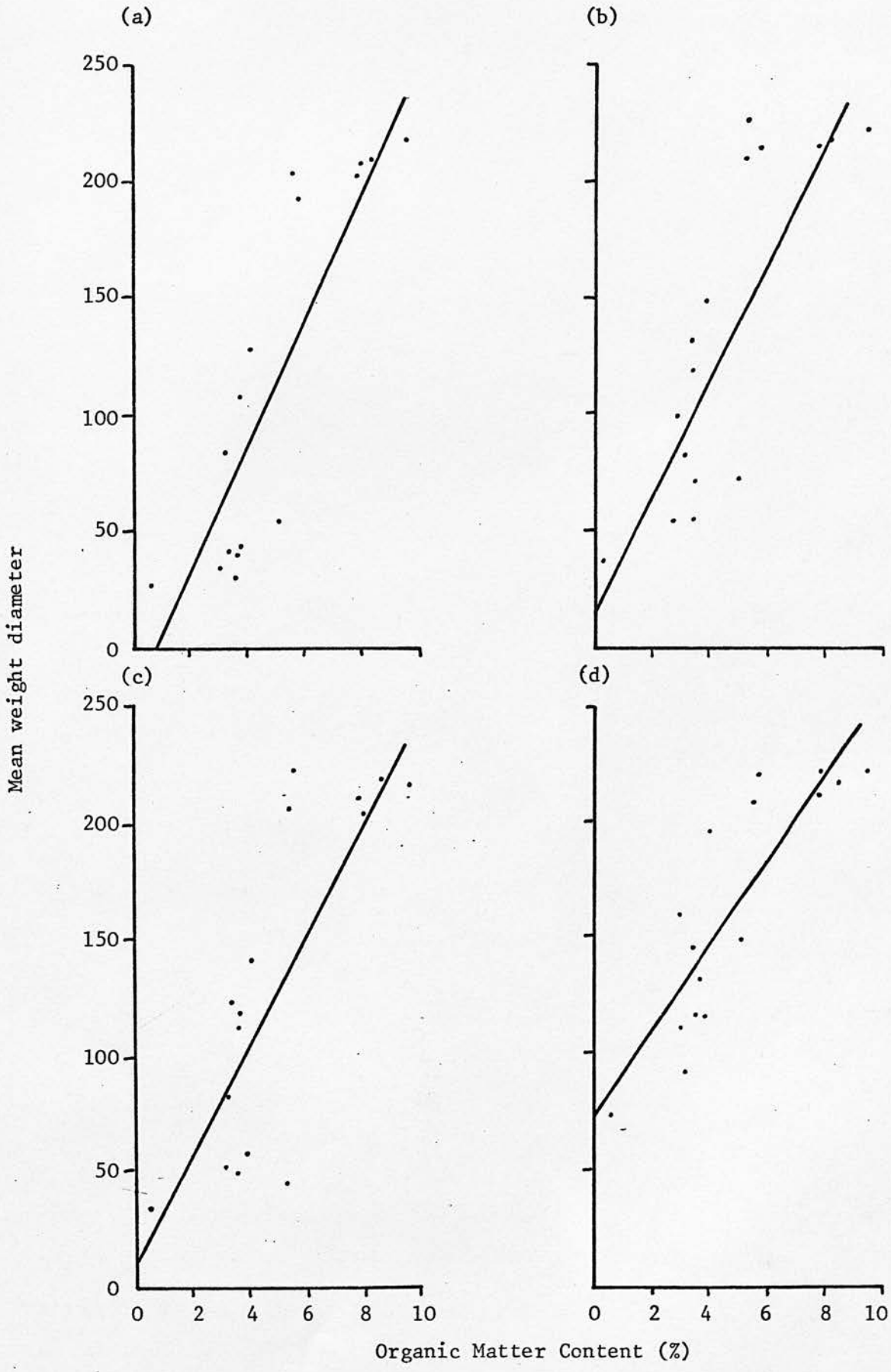
(a) no pretreatment
$y = 28x - 20$
$r = 0.857$ ***

(b) prewetted with an atomiser
$y = 25x + 13$
$r = 0.848$ ***

(c) prewetted with an atomiser and corrected for stone
$y = 25x + 5$
$r = 0.834$ ***

(d) fresh, moist aggregates
$y = 18x + 76$
$r = 0.840$ ***

Figure 12


(a)
(b)
(c)
(d)
250
200
150
100
50
0
0
2
4
6
8
10
Mean weight diameter
Organic Matter Content (%)

4.1.1.7. Discussion

All the methods tried gave results which distinguished between soil aggregates from fields with known structural problems and those from well-structured permanent pasture. The moisture characteristic method and slaking tests are qualitative and cannot be used to give an index of aggregate stability. The water drop method and leaching with decreasing concentrations of sodium chloride did not give a value for well-structured soil aggregates.

Both wet-sieving and leaching with a single concentration of sodium chloride gave results that had a highly significant correlation with organic matter content. Although leaching with sodium chloride is based upon physico-chemical principles and as such is preferable to wet-sieving (which relies on unquantifiable physical forces to disintegrate aggregates), it was decided to use wet-sieving in all further studies. The main reason for this was that wet-sieving gave easily reproducible values spread over the full range (25-240), and distinguished between all the soils tested. It was also thought that wet-sieving would be appropriate for evaluating the stability of reformed aggregates (section 4.2.).

4.1.2. The Relationship of Soil Constituents to Soil Aggregate Stability

As outlined in the Literature Review a number of factors have been suggested as being involved in the stabilisation of soil aggregates. Many studies have been carried out examining the relationship between soil constituents and soil aggregation. A large number of parameters have been used for assessing soil aggregation in these studies e.g. aggregate size distribution, dispersion ratio and the percentage of water stable aggregates. In general many

positive correlations have been reported between aggregation and soil organic matter (e.g. Rost and Rowles, 1940; Elson, 1941; Kemper and Koch, 1966), although some workers have found no relationship (e.g. Retzer and Russell, 1941). Studies of ley-fertility experiments have shown that water-stable aggregation is related to the amount of organic matter in the soil (Williams, 1975; Eagle, 1975; Low, 1975; Clement, 1975).

Rost and Rowles (1940) also found positive correlations between an aggregation ratio and clay content and total base exchange capacity. The work of Kemper and Koch (1966) affords the best comparison with the work of this study. They also used the wet-sieving technique to assess the aggregate stability of over 500 soil samples from the Western United States and Canada. The results are not directly comparable with those obtained here because they expressed their results as a percentage of water-stable aggregates. Kemper and Koch (1966) obtained relationships between aggregate stability and organic matter, total nitrogen, clay content, free iron oxides and exchangeable sodium. Soil constituents not related to aggregate stability were free aluminium oxide and calcium carbonate.

In the initial part of this study several analyses were carried out on the soils collected in 1975 (eighteen from the East of Scotland and six from Lincolnshire) to see if there was any particular soil constituent that was related to the mean weight diameter value obtained from wet-sieving. The measurements made on the soils were:- organic matter content, liquid limit, total nitrogen content, cation-exchange capacity, dithionite extractable iron, sand content and clay content. The results of these determinations are given in Tables 6 and 7. The correlation coefficients between

Table 6 The aggregate stability, organic matter content, cation - exchange capacity, total iron content, total nitrogen content, total sand content and total clay content for the soils collected in 1975

SOIL	MWD	Organic Matter (%)	CEC (meq/100g)	Iron (%)	Nitrogen (%)	Total Sand (%)	Total Clay (%)
Ha	132	3.7	13.3	2.60	0.045	51	22
Hp	225	5.6	15.8	1.80	0.031	54	23
KKa	98	3.1	16.4	2.16	-	51	23
Kp	219	8.4	24.2	2.24	0.072	51	22
Ka	148	4.0	21.1	2.28	0.036	50	23
DRa	71	3.8	17.4	1.22	0.032	73	12
PFa	53	3.0	21.0	1.92	0.035	28	30
Bg	215	8.0	28.5	1.54	-	51	18
Ba	82	3.2	15.3	2.16	0.029	49	21
Bhr	211	5.5	16.3	1.84	0.044	54	18
Bnb	72	5.1	25.8	2.52	0.046	55	18
Sa	118	3.6	18.4	1.74	0.051	10	33
Ss	37	0.5	19.0	1.26	-	6	33
Sp	223	9.5	29.7	2.60	0.045	9	32
Pa	54	3.5	18.4	1.58	0.036	37	25
Phr	215	7.9	24.5	1.40	0.064	39	26
Ra	60	2.5	21.6	1.48	0.024	45	37
Rpl	166	6.6	32.0	1.68	0.060	40	42
Rip	176	9.1	-	-	-	44	39
Da	151	3.4	26.1	2.36	0.034	31	44
Dp	200	5.5	29.0	1.56	0.075	30	42
Sx	79	1.8	-	1.60	-	53	25
Bf	74	1.9	-	1.76	-	32	24
Fa	140	2.7	-	1.08	-	71	13
Fp	166	5.8	-	0.96	-	68	12

Table 7 Results for liquid limit, plastic limit, plastic index and particle size analysis of soils collected in 1975

SOIL	1 Liquid Limit	2 Plastic Limit	3 Plastic Index	4 % Coarse Sand	5 % Fine Sand	6 % Silt	7 % Clay	8 Textural Class
Ha	37	19	18	22	31	25	22	sandy clay loam
Hp	45	31	14	23	31	25	23	
KKa	31	21	10	20	31	26	23	sandy clay loam
Kp	57	38	19	19	32	27	22	
Ka	40	24	16	20	30	27	23	
DRa	27	20	7	37	36	15	12	sandy loam
PFa	41	24	17	3	25	42	30	clay loam
Ba	32	22	10	18	31	30	21	sandy clay loam
Bhr	39	30	9	31	23	28	18	
Sa	55	31	24	1	9	57	33	silty clay loam
Ss	48	28	20	0	6	61	33	
Sp	64	46	18	3	6	59	32	
Pa	41	26	15	12	25	38	25	sandy clay loam
Phr	53	39	14	15	24	35	26	
Ra	40	19	21	21	24	18	37	sandy clay loam
Rpl	72	48	24	17	22	19	42	
Da	51	26	25	21	10	26	44	sandy clay loam
Dp	60	45	15	17	13	28	42	
Fa	29	21	8	37	34	16	13	sandy loam
Fp	39	29	10	37	31	20	12	
Sx	30	17	13	35	18	22	25	sandy clay loam
Bf	31	21	10	10	22	44	24	clay loam

the various soil components and the mean weight diameter value have been calculated and are discussed below.

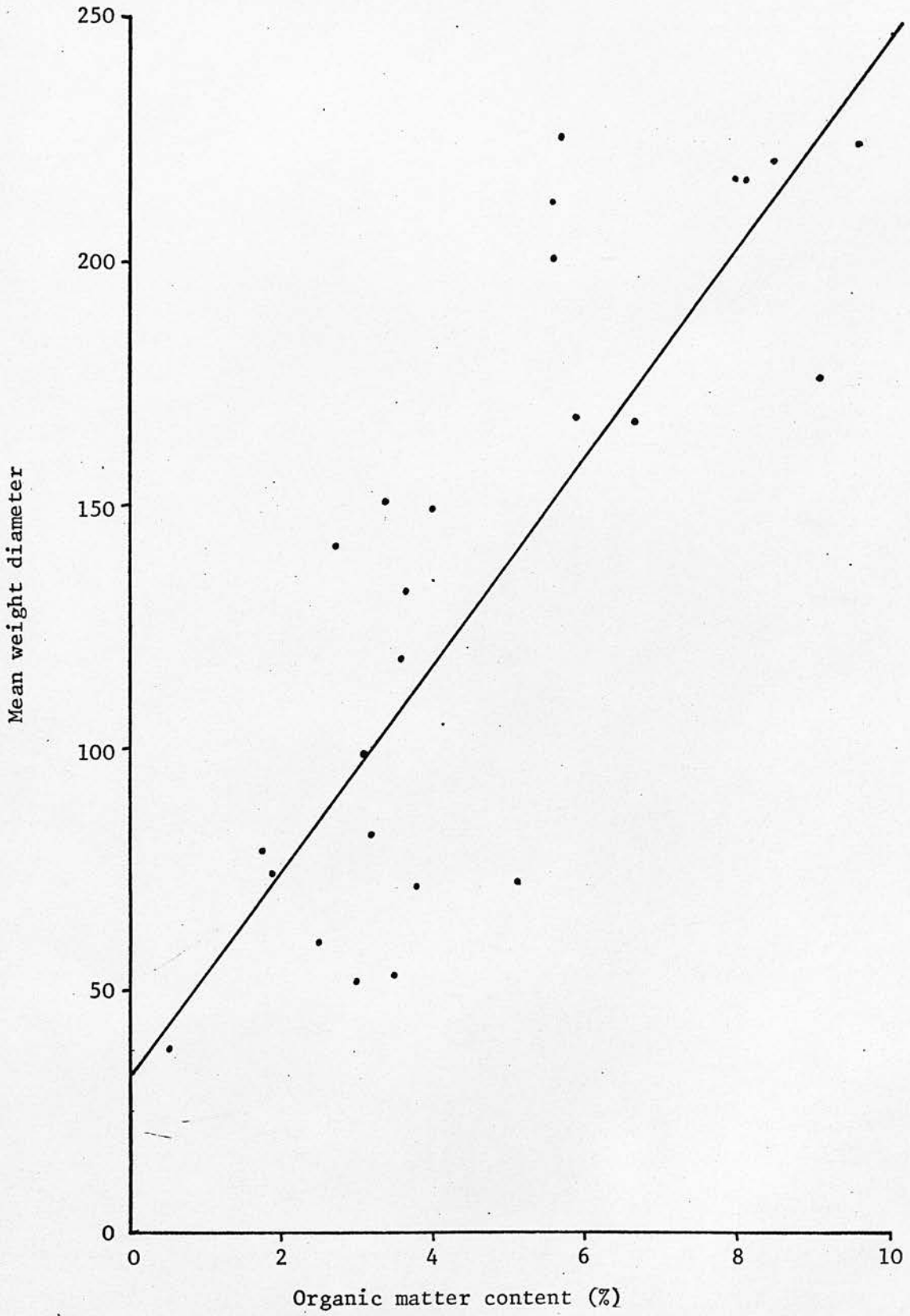
Organic matter. The correlation coefficient for aggregate stability and organic matter content is 0.813, which is highly significant at the 0.1% level (M.W.D. = 21 x OM% + 34). This is the most significant correlation of those calculated, and the data is plotted in Figure 13. The results indicate that aggregate stability (represented as M.W.D.) and organic matter have a linear relationship over the range studied i.e. an increase in organic matter would be associated with an increase in aggregate stability.

Although a linear relationship has been imposed upon the data, the maximum M.W.D. obtainable with the wet-sieving apparatus used in this study is 240. Consequently the curve must flatten off at this value and increases in organic matter beyond the level at which this is achieved will not be associated with increases in mean weight diameter. A possible explanation could be that all the potential bonding mechanisms between clay and organic colloids have been fulfilled. Therefore, any extra organic material will have no affect on the stability of soil aggregates.

It must also be pointed out that the curve obtained in Figure 13 could be changed by wet-sieving at a faster rate or for a longer period. For example, if wet-sieving were carried out for ten minutes instead of four, it is possible that the aggregates from soils with high organic contents would have a lower mean weight diameter value. In fact this could be a suitable way of distinguishing between the high organic matter soils which had similar aggregate stability values after four minutes wet-sieving. A four minute wet-sieving time was employed in this study because it was found that when arable soils were wet-sieved for ten minutes, the mean weight diameter

Figure 13 Plot of Organic Matter Content against Aggregate Stability (MWD) for the Initial soils.

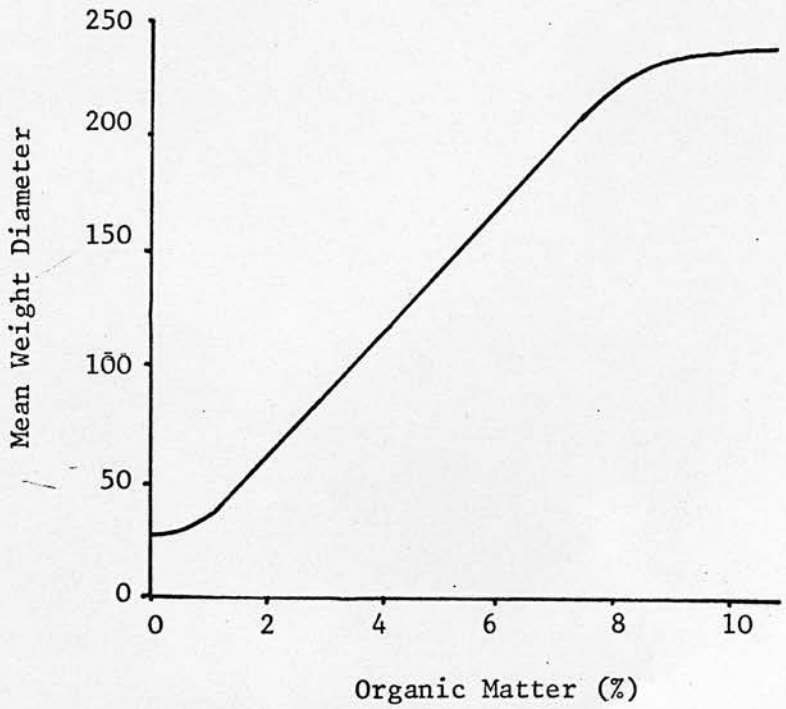
($y = 21x + 34$; $r = 0.813^{***}$)



values were all very low. This compression of the values to the bottom of the curve is not consistent with observations made in the field on the stability of these soils.

It also seems reasonable to suggest that the graph of mean weight diameter and organic matter will not be linear at very low organic matter levels. When organic colloids are present in soils in relatively small amounts (e.g. < 1%), whilst clay-organic interactions occur, they may not be sufficient to bring about the stabilisation of soil aggregates greater than 0.5mm. (Stable aggregates smaller than 0.5mm will not be detected using the wet-sieving apparatus). As the organic matter content is increased a "threshold value" is reached when stabilisation of aggregates occurs. Above this value extra organic matter increments will continue to promote aggregate stability, and give a linear relationship over a certain range of organic matter contents (e.g. 1-8%). This type of arguement would give an S-type curve.

Figure 14. Theoretical curve for organic matter and aggregate stability



Indeed, Kemper and Koch (1966) found that decreases in organic matter below 1% were associated with large reductions in aggregate stability, indicating that there may be a threshold effect. The S-type curve is linear over the range of organic matter values found in a large number of agricultural situations. Therefore, although treating the relationship as wholly linear may not be correct, because the range of organic matter levels of the soils used in this study falls in the central portion of the S-type curve, it is a good approximation.

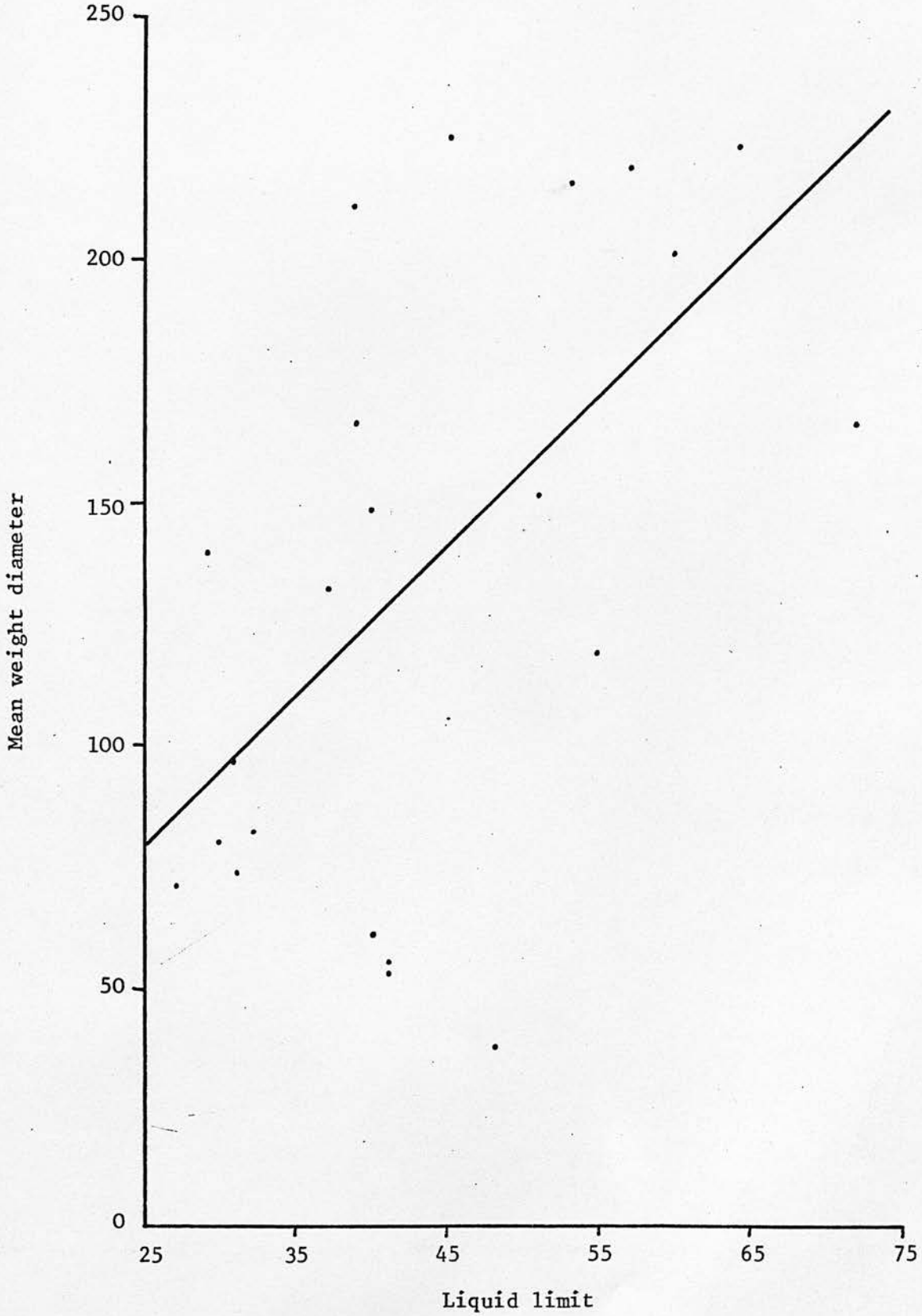
Liquid limit. Towner (1973) suggested that measurements made with the cone penetrometer could be related to soil physical properties. Therefore, liquid limit measurements were made on the soils collected in 1975 from the East of Scotland and Lincolnshire. The results obtained for liquid limit using the cone penetrometer together with the plastic limit, plastic index and particle size analysis are presented in Table 7. The organic matter content and aggregate stability (M.W.D.) of these soils are given in Table 6.

The cone penetrometer gave reproducible results for the liquid limit determination that agreed well with measurements made with the Cassegrande apparatus. The plastic limit of the soil was also determined and by subtracting this value from the liquid limit, the plastic index was obtained.

The relationship between liquid limit and aggregate stability is shown in Figure 15. There is quite a large scatter of the points, and this is reflected in the correlation coefficient, 0.600. This value is significant at the 1% level, showing there is a positive relationship between liquid limit and aggregate stability. However, this relationship was not as good as that obtained between organic

Figure 15 Plot of Liquid Limit against Aggregate Stability for the Initial Soils collected

($y = 3x - 4$; $r = 0.600^{**}$)



matter and aggregate stability, which had a correlation coefficient of 0.813 for the same soils (significant at the 0.1% level). The liquid limit is well related to the soil organic matter level, having a correlation coefficient of 0.718 which is significant at the 0.1% level. This indicates that the correlation between liquid limit and aggregate stability arises because both parameters are related to the organic matter content. Therefore, the liquid limit determination was not used to assess aggregate stability, although it may prove a useful measure for soils of the same textural class.

Plastic limit and plastic index were not correlated with aggregate stability, but were positively related to organic matter content.

Total nitrogen. The total nitrogen content of the soil was also found to give a significant correlation with aggregate stability. The correlation coefficient is 0.581, which is significant at the 5% level (M.W.D. = 2553 x N% + 27). The fact that total nitrogen is related to aggregate stability in this study, that of Kemper and Koch (1966) and that of Williams (1970) suggests that humic substances are involved in soil aggregation. This is based upon the knowledge that a very large proportion of the nitrogen in the soil is incorporated in humic polymers.

Clay content. Kemper and Koch (1966) found that the clay content had a linear relationship with aggregate stability. The correlation coefficient for clay content and aggregate stability in this study was 0.078, which indicates there is no relationship at all. Kemper and Koch (1966) had a wide range of clay contents (10-90%) in their soils, whereas the soils sampled in this study were mainly sandy clay loams.

Sand content. The correlation for total sand content (>0.02mm) and aggregate stability was equally poor, having a correlation coefficient of 0.071. If the relationship between clay and aggregate stability (Kemper and Koch, 1966) is correct then it would be expected that a negative correlation be obtained for the total sand content. Some workers (Williams, 1970) have shown that a large proportion of coarse particles in soils (especially those with less than 2% organic matter) can give rise to very unstable soil aggregates.

Total iron content. The dithionite extraction used in this study would give a similar measure of the free and surface iron oxides as that of Kemper and Koch (1966). However, the correlation coefficient between total iron and aggregate stability is 0.110, showing there is no relationship, whereas Kemper and Koch (1966) obtained a good correlation.

Cation-exchange capacity. A correlation coefficient of 0.408 was obtained for aggregate stability and cation-exchange capacity; this is not significant. The exchangeable calcium and sodium were also determined on the same soils. Neither of these two exchangeable bases gave a significant correlation with soil aggregate stability.

This initial work has shown that organic matter is one of the major factors involved in the stabilisation of soil aggregates. Therefore a more detailed study of the relationship between organic matter and aggregate stability was undertaken.

4.1.3. Relationship Between Soil Organic Matter and Its Components to Soil Aggregate Stability

In addition to the soils collected in 1975 (Appendix, Tables A1 and A2), soils from Essex and Warwickshire (Appendix, Table A2) and soils of the Kilmarnock (Appendix, Table A3), Humbie (Appendix,

Table A4), Stirling (Appendix, Table A5) and Winton (Appendix, Table A6) soil series, were sampled. A lateritic soil collected from the Cerrado of Brazil was also included (Appendix, Table A1). This gave a total of one hundred and thirteen soils, which included twenty seven from England and eighty five from the East of Scotland.

The soils collected in 1976, 1977 and 1978 from the East of Scotland were sampled from five soil series, all heavier textured soils and known to suffer from structural problems under some arable conditions. It was thought that by collecting soils from a variety of cropping systems on the same soil series, and thus eliminating the variable of textural difference, the results would reveal one or more factors involved in soil aggregation.

Additional soils were also collected from the east and west of England to obtain a wider cross-section of heavier textured soils. Many of the soils from Essex have low organic matter contents compared to Scottish soils, due to the intensive continuous cultivation systems imposed upon them and climatic conditions. The soils from Warwickshire are very difficult to farm because of structural and water management problems.

In the preceding section several determinations were carried out on the soils collected in 1975 (Table 6). Calculation of the correlation coefficients between aggregate stability (measured by wet-sieving) and these parameters, gave a highly significant correlation for the organic matter content. Since, this was the best relationship obtained, it was decided to concentrate upon the influence of organic matter and its constituents upon aggregate stability.

Therefore, all the soils sampled had the following measurements made upon them:-

1. Aggregate stability, presented as a mean weight diameter value
2. Total carbon content (%)
3. Total organic matter (%)
4. Total polysaccharide content (%)
5. Optical density reading of 0.1M sodium pyrophosphate extractable humic and fulvic acids
6. Optical density reading of 0.5M sodium hydroxide extractable humic and fulvic acids, after extraction with pyrophosphate
7. The total of 5 and 6
8 Optical density reading of 0.5M sodium hydroxide extractable humic and fulvic acids on a separate soil sample

The results of these determinations are given in the Appendix (Tables A7 - A11) for soils collected from the East of Scotland in 1975, English soils, Kilmarnock and Humbie soil series, Stirling soil series and Winton soil series respectively. The correlation coefficients have been calculated between the mean weight diameter value and organic matter and its constituents (determinations 3,4,5,6,7 and 8 above), for all the soils and for the soils in a particular Table or soil series. The values of the correlation coefficients for each of these relationships are given in Table 8. To illustrate the type of results obtained graphs have been plotted for the most and least significant correlations between each organic matter constituent and aggregate stability (Figures 16-21). The regression equations have been calculated for all the relationships and are given in the Appendix (Table A12).

The values of the individual correlations are discussed below.

Table 8

Correlation coefficients for mean weight diameter and organic matter constituents

Soil group of series	Organic Matter (3)	Polysaccharide Content (4)	Pyrophosphate extractable humic acid (5)	Sodium hydroxide extractable humic acid (6)	Sum of 5 & 6 (7)	Sodium hydroxide extractable humic acid only (8)
ALL SOILS n = 113	*** .6630	*** .7113	*** .5258	*** .6149	*** .6384	*** .6493
EAST SCOTLAND n = 18	*** .8264	*** .7552	** .6482	*** .8341	*** .8344	*** .8625
ENGLISH n = 27	*** .7521	*** .7329	*** .6879	*** .7178	*** .8040	*** .7468
KILMARNOCK n = 13	** .7439	*** .8811	** .6982	** .6900	* .5975	* .6573
HUMBIE n = 14	*** .7743	** .7106	** .7034	** .7463	** .7601	*** .7668
STIRLING n = 27	*** .8674	*** .7916	*** .6068	*** .7642	*** .7152	*** .7018
WINTON n = 21	*** .7057	*** .8906	.2253	** .6136	* .5037	* .5175

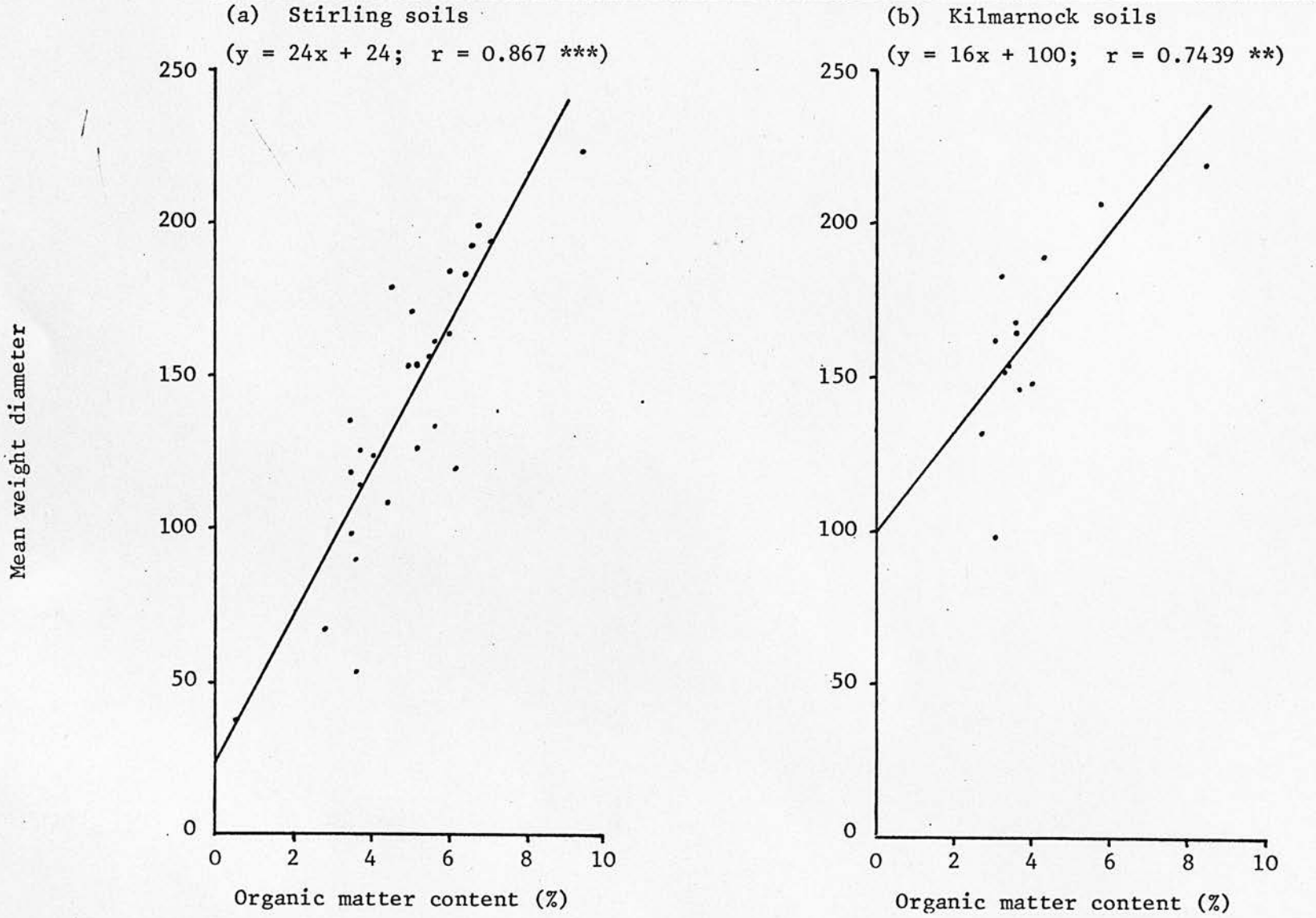
*** significant at the 0.1% level
** significant at the 1% level
* significant at the 5% level

Organic matter. The carbon content of the soils was determined by the wet-oxidation method (column 2 of Tables A7-A11), and this value was multiplied by 1.74 to give the organic matter content (column 3 of Tables A7-A11). The correlation coefficients between the organic matter content and aggregate stability (represented by M.W.D. - column 1 of Tables A7-A11) were calculated. Six out of the seven correlation coefficients presented in Table 8 for organic matter and aggregate stability are significant at the 0.1% level. The seventh one, that of the Kilmarnock soils, is significant at the 1% level. These results indicate that soil organic matter has a linear relationship with aggregate stability for all the soils studied. The plots of organic matter against mean weight diameter are shown in Figure 16 for the Stirling soils (a) and the Kilmarnock soils (b).

In the graph for the Stirling soils (Fig. 16(a)) the points are closely grouped along the calculated regression line, illustrating the statement above, i.e. that aggregate stability is dependent upon the organic matter content of the soil. Although the results of the Kilmarnock soils gave the poorest correlation coefficient for organic matter and mean weight diameter, they are still good. The fact that the correlation is not as significant is reflected in the greater spread of the points from the regression line and also by the intercept on the y axis (Fig. 16(b)). The intercept value of 100 indicates that this would be the mean weight diameter value of a soil with no organic matter. This cannot be correct because one of the points plotted was for a soil with 3.1% organic matter and a M.W.D. of 91. By comparison, the regression line of the Stirling soils cut the y axis at a value of 24. This indicates that a soil with no organic matter would have no stable aggregates, a more sensible result.

Figure 16

Plots of Organic Matter Content against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations



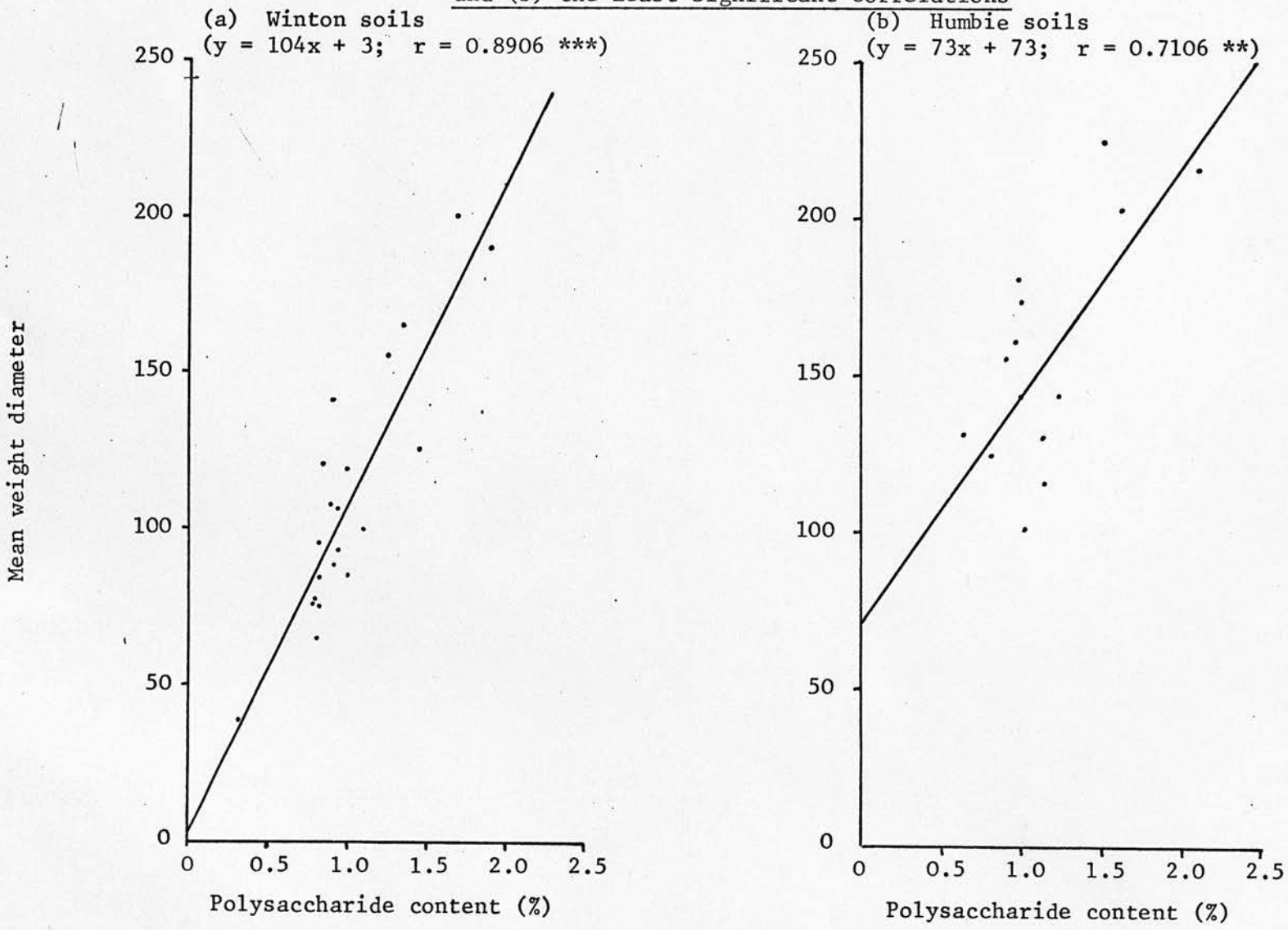
In the previous section it was stated that the regression analysis might not be the most appropriate method of treating the data. It was suggested that an S-type curve (Fig. 14) might give a better fit to the data. If the graphs in Fig. 16(a) and (b) are examined closely with respect to imposing an S-type curve, it would appear that this is a possibility in both curves. An S-type curve could also be imposed on the graphs of organic matter and mean weight diameter of the other soil groups (the regression equations are given in Table A12 of the Appendix).

However, since the majority of the organic matter values for the soils sampled in this study fall on the straight line part of the S-type curve, the regression line gives a very good approximation to the relationship as it applies to soils in agricultural situations. This is reflected through six out of seven correlation coefficients being highly significant.

Polysaccharide content. The polysaccharide content of the soils was determined, after hydrolysis with two strengths of sulphuric acid, by the concentrated sulphuric acid-phenol method using glucose as the standard. Other monosaccharides, namely mannose and xylose, were used as standards, but these were found to give similar calibrations to that of glucose. The results of the polysaccharide determinations are given in column 4 of Tables A7-A11 of the Appendix. The correlation coefficients calculated between M.W.D. and polysaccharide content are given in Table 8. Six of the seven correlations were significant at the 0.1% level (highly significant) whilst the Humbie soils give a correlation coefficient of 0.7106 (significant at the 1% level). Graphs have been plotted (Figure 17) of polysaccharide content against M.W.D. for the Winton soils (Fig. 17(a)) and the Humbie soils (Fig.

Figure 17

Plots of Polysaccharide Content against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations



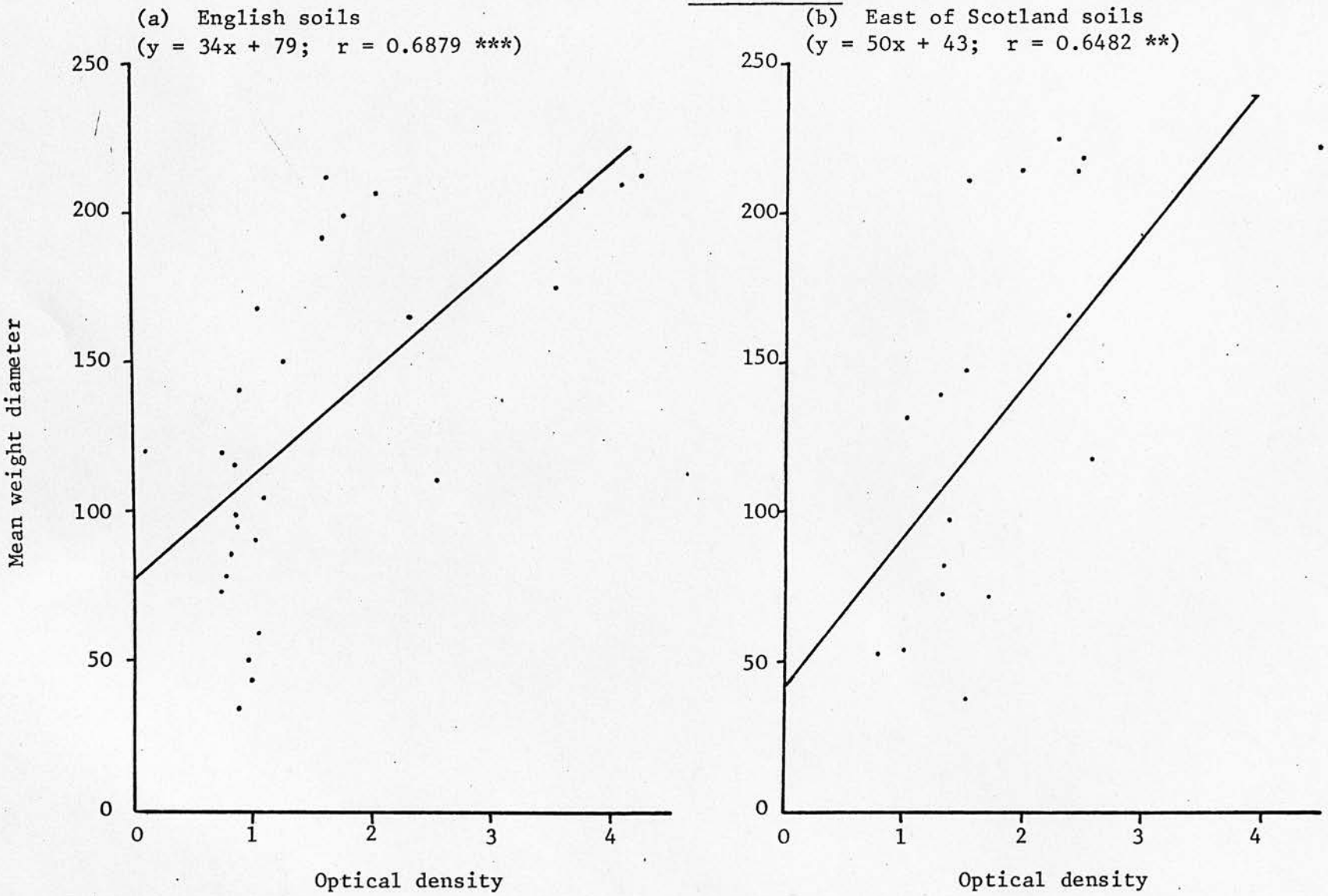
17(b)). Comparing the correlation coefficients of organic matter and M.W.D. with those of polysaccharide and M.W.D. for each group of soils, four out of seven of the O.M.-M.W.D. correlation coefficients are higher than those for polysaccharide-M.W.D. However, the correlation coefficient for polysaccharide-M.W.D. is greater than that of O.M.-M.W.D. for all the soils. This indicates that the polysaccharide content of a soil has a major role in determining the stability of the soil aggregates. This agrees with the conclusions of Toogood and Lynch (1959), who found that M.W.D. values were related to polysaccharide content of the Canadian soils studied.

Pyrophosphate extractable humic acid. The values quoted in column 5 of Table A7-A11 of the Appendix are optical density values. These were obtained by measuring the optical density of the humic acid solution extracted with 0.1M sodium pyrophosphate from a 1g sample of soil. The correlation coefficients calculated for the pyrophosphate extractable humic acid (pyro H.A) are presented in Table 8. In all cases, the pyro H.A.-M.W.D. correlation coefficient is lower than that of O.M.-M.W.D. and polysaccharide-M.W.D. for a group of soils. Despite this fact, three correlation coefficients (All soils, English and Stirling) are significant at the 0.1% level. Three correlation coefficients are significant at the 1% level, and that of the Winton soils was not significant. Although the relationship between pyro H.A. and aggregate stability is not as good as that of organic matter or polysaccharide, the three star correlation for All Soils indicates that this humic acid extract is involved in aggregation.

The plots (Figure 18) of pyrophosphate extractable humic acid against M.W.D. illustrate this point. Both Fig. 18(a) and Fig 18(b) have a much greater spread of points from the regression

Figure 18

Plots of Pyrophosphate Extractable Humic Acid against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations



line than the graphs of Fig. 16 or 17.

Sodium hydroxide extractable humic acid. After the pyrophosphate extract was decanted the same soil sample was extracted with 0.5M sodium hydroxide. The optical density of the supernatant humic acid solution is given in column 6 of Tables A7-A11 of the Appendix. The correlation coefficients calculated between aggregate stability (MWD) and sodium hydroxide extractable humic acid are given in Table 8.

Four correlations are significant at the 0.1% level and three are significant at the 1% level, indicating that this organic matter fraction is involved in the stabilisation of soil aggregates. In general the correlations are better than those between aggregate stability and pyrophosphate extractable humic acid, but not as good as those between aggregate stability and total organic matter content or polysaccharide content. If humic acid is involved in the stabilisation of soil aggregates it might be expected that the pyrophosphate extractable humic acid is not as well correlated with mean weight diameter as the subsequent sodium hydroxide extract.

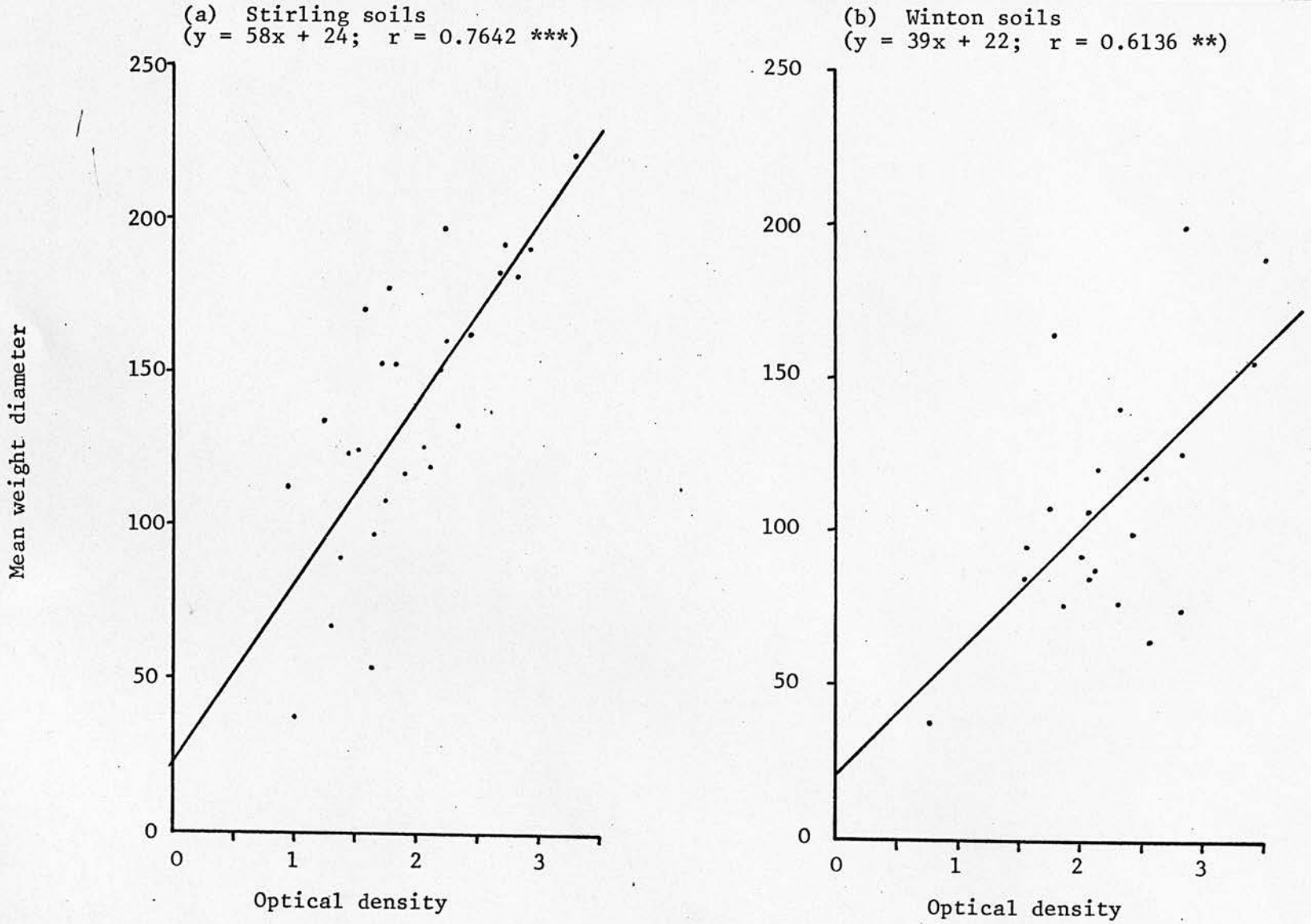
Pyrophosphate is a relatively mild extractant compared with sodium hydroxide, and would be expected to extract the lower molecular weight, more oxidised humic acid that is not strongly adsorbed by inorganic particles. The subsequent, harsher extraction with sodium hydroxide would contain the higher molecular weight, less oxidised humic acid, and humic acid that was more strongly adsorbed to clay and oxide particles. It would appear that this type of humic acid fraction has a more significant correlation with aggregate stability than the lower molecular weight, more oxidised humic acid fraction does.

This is consistent with the bonding mechanisms of clay organic colloids put forward in section 2.3. A high molecular weight organic molecule with several sidechains would be far more capable of bonding to several clay particles than a low molecular weight molecule.

The plots of sodium hydroxide extractable humic acid against mean weight diameter are shown in Figure 19. The correlation coefficient for the Stirling soils (Fig. 19(a)) is 0.7642, which is significant at the 0.1% level. The relationship with the poorest correlation is that of the Winton soils (Fig. 19(b)) which has a correlation coefficient of 0.6136 that is significant at the 1% level.

Sum of the pyrophosphate and sodium hydroxide extractable humic acid. Column 7 of Tables A7-A11 of the Appendix gives the sum of the optical densities of the humic acid solutions extracted with pyrophosphate (column 5) and sodium hydroxide (column 6). As both these extractions were carried out on the same soil sample, this value is a measure of the total humic acid extracted. Four of the correlation coefficients calculated between aggregate stability (MWD) and the sum of the pyrophosphate and sodium hydroxide extractions are significant at the 0.1% level, one is significant at the 1% level and two are significant at the 5% level (Table 8). As would be expected the soil groups that gave the best correlations for the individual humic acid extracts have given the best correlations for the sum of these extracts, and vice versa. However, for a given group of soils, the correlation coefficient of the sum of the two extracts is better in six out of seven cases than those for pyrophosphate extraction alone, and better in four out of seven cases for the sodium hydroxide extraction alone.

Figure 19 Plots of Sodium Hydroxide Extractable Humic Acid (after pyrophosphate extraction) against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations



The graphs plotting the best (Fig. 20(a)) correlation and the poorest correlation (Fig. 20(b)) between the sum of the pyrophosphate and sodium hydroxide extractable humic acid and aggregate stability are shown in Figure 20. The graph for the English soils has a large spread of points from the regression line although the correlation coefficient (0.8040) is significant at the 0.1% level. The mean weight diameter ranges from 35 to 141 over as small an optical density range as 1.22 to 1.44 (Table A8).

Sodium hydroxide extractable humic acid (on a separate soil sample). The optical density of the humic acid extracted from a separate 1g soil sample with 0.5M sodium hydroxide is given in column 8 of Tables A7-A11 of the Appendix. Comparing the optical density values in column 8 with those of the sum of pyrophosphate and sodium hydroxide extractions on the same soil sample (column 7), it can be seen that the value in column 7 is always the greater. Stating this another way, a sequential extraction of sodium pyrophosphate and sodium hydroxide extracts more humic acid than a single sodium hydroxide extraction. The reason for this is that the sodium pyrophosphate complexes iron and aluminium in the soil and removes it. Therefore when sodium hydroxide subsequently is added humic acid which was held tightly because of iron and aluminium is then able to be extracted.

Five of the seven correlation coefficients calculated (Table 8) between aggregate stability (MWD) and the sodium hydroxide (only) extractable humic acid are significant at the 0.1% level. The other two correlation coefficients are significant at the 5% level. The graphs plotting the best correlation (East of Scotland soils) and the poorest correlation (Winton soils) are shown in Figure 21.

Figure 20 Plots of the Sum of Pyrophosphate Extractable and Sodium Hydroxide Extractable Humic Acid against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations

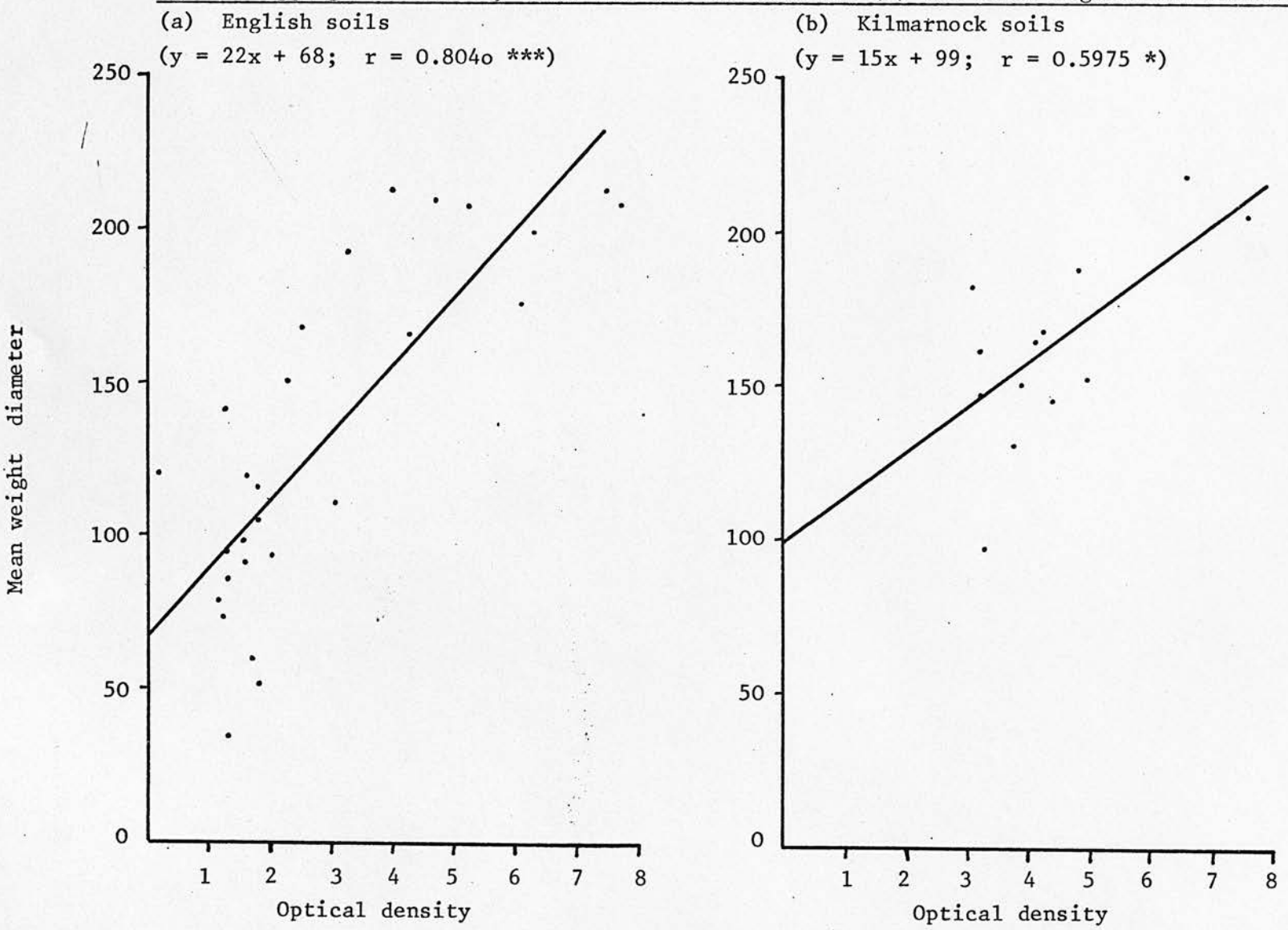
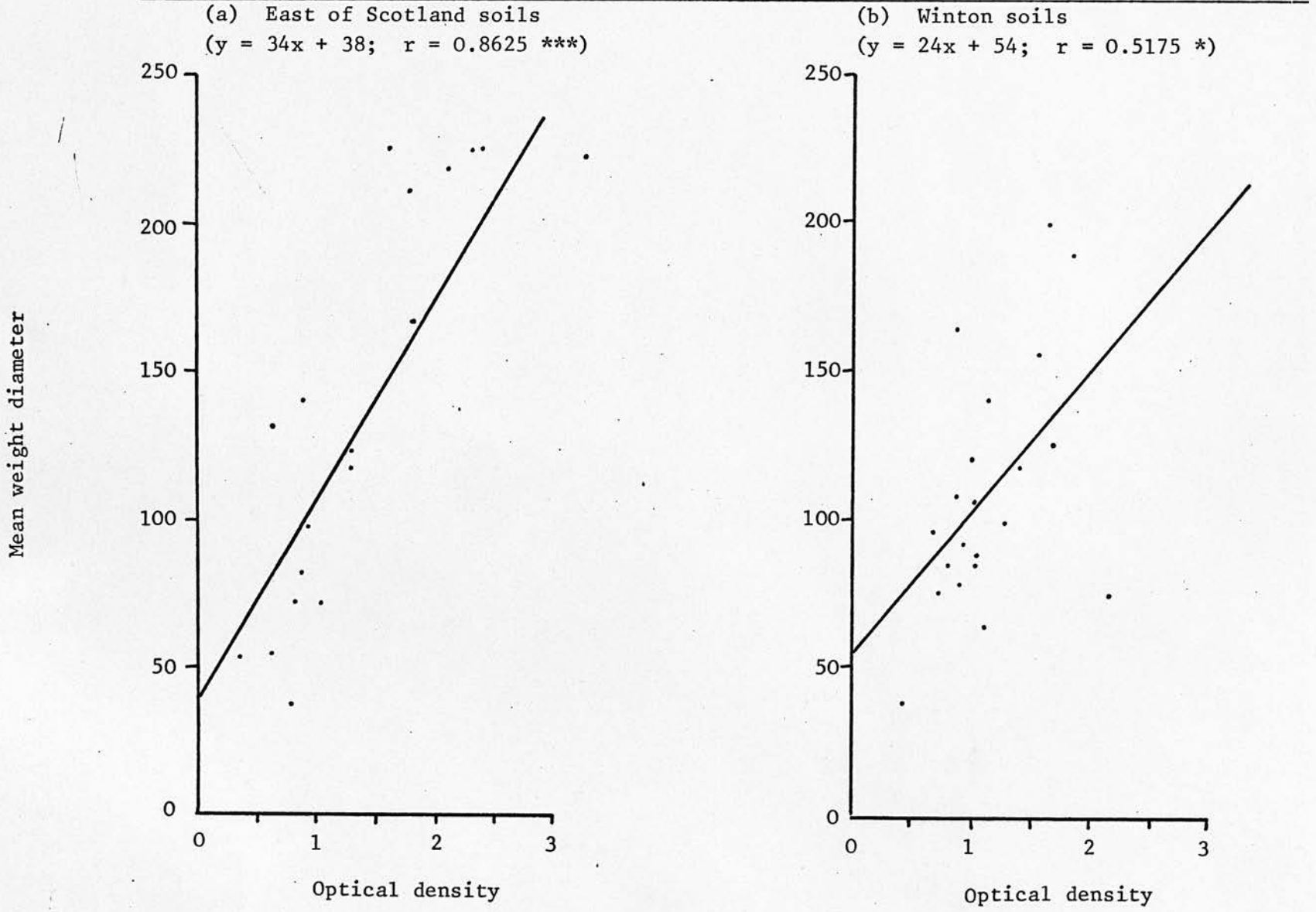


Figure 21 Plots of Sodium Hydroxide Extractable Humic Acid (from a separate soil sample) against Aggregate Stability (MWD) for (a) the Most and (b) the Least Significant Correlations



General discussion. In section 4.1.2. it was found that there was a highly significant correlation between the total soil organic matter content and aggregate stability (represented by MWD). Several determinations were then made in this part of the study to see if one of the constituents of the organic matter was involved in the stabilisation of soil aggregates. The results obtained indicate that at least two of the soil organic matter fractions, namely polysaccharides and humic substances, are involved in the stabilisation of soil aggregates. This is shown through the correlation coefficents calculated (Table 8) between aggregate stability and organic matter/organic matter constituents being highly significant at the 0.1% level, for All Soils (113).

In all the analyses carried out the organic material that is not adsorbed, and therefore of little use in stabilisation, was determined along with the active material. Taking this into consideration the values obtained for the correlation coefficients were very good. If the inactive organic material (e.g. decomposing plant and animal residues, free humic acid, etc.) was removed from the soil before each determination was made, then the correlations may be even better.

An attempt was made to remove a "light" organic fraction by flotation in water and by flotation in carbon tetrachloride/manoxol solution. Neither of these methods gave a total separation of the free organic material from the soil. Although the use of a surfactant (manoxol) in carbon tetrachloride gave more organic material than flotation in water, it does not separate the "heavier" organic material which is not associated with mineral particles. In these experiments the "heavy" organic material was seen to take a much longer time to settle than the mineral particles.

Although the correlation coefficient between polysaccharide content and aggregate stability for All Soils was the highest value obtained (0.7113), it was not always the best correlation for the separate soil groups. Therefore polysaccharide content cannot be the sole agent involved in aggregate stabilisation. Indeed, from the results obtained it would appear that stabilisation of soil aggregates is brought about by both components and may be the result of a complex interaction between the polysaccharide and humic substances.

For example, consider the correlation coefficients obtained between the organic matter constituents and aggregate stability of the Kilmarnock and Winton soil series (Table 8). These two soil series gave the lowest set of correlation coefficients between humic acid extractions and aggregate stability. In one case, the pyrophosphate extraction of the Winton soils gave no correlation at all with aggregate stability. However these two soil series also had the highest correlation coefficients between polysaccharide content and aggregate stability. In the other soil groups the humic acid extractions were as well correlated, if not better, with aggregate stability as the polysaccharide content.

It has been suggested by various workers (Acton et al, 1963; Greenland et al, 1964; Griffiths and Jones, 1965; Griffiths and Burns, 1972) that polysaccharide material is capable of bringing about the formation of stable soil aggregates. The results of this study indicate that polysaccharide material is also involved in the process of aggregate stabilisation. This is not consistent with the knowledge that polysaccharides are susceptible to microbial attack. However, it is possible that the polysaccharides are pro-

tected from microorganisms, through adsorption by clay minerals or through the deposition of coatings of iron or aluminium oxides on the polysaccharide. Griffiths and Burns (1972) suggested that phenolic compounds could be implicated in the stabilisation of soil aggregates, possibly through the protection of the polysaccharide material or through the stabilisation of the structure formed by the polysaccharide.

The correlations between the humic acid extracts and aggregate stability obtained in this study indicate that humic substances are involved in stabilising soil aggregates. The fact that the pyrophosphate extractions gave correlations for the soil groups which were not as good as those of the sodium hydroxide extractions, suggests that it is the humic acid which is more strongly adsorbed that is having the major effect on stabilising soil aggregates.

A possible explanation could be that the polysaccharide is important in the initial stages of aggregation. It brings about the formation of aggregates and stabilises them to some extent. The second phase would be the stabilisation of these structures by humic acid, either through protection of the polysaccharide or more likely through their adsorption by adjacent clay mineral particles. In the humic adsorption mechanism the polysaccharide would probably be degraded eventually by microorganisms and disappear from the soil environment. This would also occur if humic acid were not adsorbed, with the resulting loss in structure. At some future date with a fresh input of organic material the process could start again.

In the second part of the study the role of polysaccharides and humic substances in forming and stabilising soil aggregates will be examined in the laboratory. By making additions of organic matter constituents to soil with no aggregates, information may be

obtained concerning the mechanisms of aggregate formation and stabilisation.

4.2. LABORATORY STUDIES EXAMINING THE ROLES OF VARIOUS ORGANIC COLLOIDS ON THE FORMATION AND STABILISATION OF SOIL AGGREGATES

4.2.1. Introduction

The main reason for choosing the Stirling soil for the experiments carried out in this part of the study was that the subsoil had a low organic matter content and a very poor soil structure. This was shown by the mean weight diameter value of the natural aggregates being 37 $\pm$ 4; a soil with no stable aggregates would have a value of 25. Therefore organic additions could be made to this soil and the results compared with the permanent pasture soil (a high organic matter content and well structured stable soil aggregates) at the other end of the scale, and with the arable soil which is intermediate between these two extremes. Another factor leading to the use of these three soils was that the soils were collected from an area of uniform geology and topography, and sampled from adjacent sites either side of a boundary fence. This ensured that the pasture and arable soil samples were derived from the same parent material and differ only because of the cultivation and cropping systems imposed upon them. The subsoil was sampled at the same site as the arable soil. The Kilmarnock, Beccles and Ragdale series were used mainly to see if the results obtained with the Stirling soils were consistent with other soil series.

4.2.2. Preliminary Adsorption Experiments

As part of this study it was proposed to adsorb humic acid onto the soil and examine the effect such an interaction has on the

stability of the reformed aggregates. The final mean weight diameter determination of these experiments is destructive making it difficult to carry out other measurements on the same sample. Therefore, before undertaking such a study, it was necessary to conduct a series of test-tube experiments to determine the optimum conditions for adsorption to take place, and the amount of organic material adsorbed under the conditions used. The conditions of the test-tube experiments were made as similar as possible to those used in the large scale adsorptions. For example, the weight of humic acid added per gram of soil was the same in both experiments.

Several workers (e.g. Evans and Russell, 1959) have studied the effect of pH on the adsorption of humic acid and have shown that there is a fall in adsorption as the pH rises from 3 to 6, this fall being especially marked from pH 3.5 to 4.5 However, at low pH values precipitation of the humic acid can occur. Centrifugation experiments with humic acid showed that precipitation had not occurred at pH 3.5, but precipitates were observed at pH values below this. Therefore, pH 3.5 was chosen as the pH at which maximum adsorption of the humic acid would occur without precipitation. A second set of adsorptions were carried out at neutrality (pH7).

The results of the adsorption studies of Stirling arable and Stirling subsoil at pH 3.5 and 7.0 are presented in Table 9. The calcium and sodium saturated soil used were prepared by the method described in section 3.2.2.6. The humic acid used for this study was extracted from a Fen peat soil with 0.5M sodium hydroxide as described in section 3.2.2.1.

The values quoted in Table 9 are the mean values of four experiments, each carried out in duplicate. The figures for the percentage of humic acid adsorbed was much greater at pH 3.5 than 7.0.

The percentage adsorbed at pH7 ranges from 3 to 8%, whereas at pH 3.5 the values range from 71-96%. The amount of humic acid adsorbed at pH7 varied very slightly, ± 1%, but at pH 3.5 there was a much greater variation in the results. The variation in the humic acid adsorbed by Stirling arable (± 10%) was less than that of Stirling subsoil (± 15%). This variation of adsorption values at pH 3.5 could be due to the problems of obtaining uniform 5g soil samples. Since it is the clay fraction which is active in adsorbing organic colloids (MacEwan, 1948; Evans and Russell, 1959; Greenland, 1965a and b; Giles et al, 1960), a small change in the particle size distribution of the soil sample could lead to large changes in the amount of humic acid adsorbed. A second explanation, possibly more likely, is that the variation in adsorption values was due to small variations in pH. Addition of 1M acid to the humic acid/soil mixture does not adjust the system to an equilibrium pH of 3.5 immediately. Although the pH was monitored until the pH appeared stable and again after half an hour of shaking it was still possible for the pH to drift by 0.2 of a unit from the required value. Such a change of pH could account for the variation in adsorption values, because the decrease in adsorption of humic acid is especially marked as the pH rises from 3.5 to 4.5.

The values for the amount of humic acid adsorbed at pH 3.5 by S_sCa^{2+} and S_aCa^{2+} were greater than those of S_sNa^{+}. When sodium saturated humic acid is added to calcium saturated soil, the calcium ions would be selectively taken up by the humic acid, displacing the sodium ions. If sufficient Ca^{2+} were taken up by the humic acid for calcium to be the dominant cation, then precipitation of the humic acid could occur. This coprecipitation of humic acid is not distinguishable from adsorption. In an all sodium system this phenomenon

Table 9 The absorbance Values and the % of humic acid adsorbed, when 2mg/ml humic acid solutions were added to 5g samples of sodium saturated and natural soil of Stirling arable and Stirling subsoil at pH 3.5 and 7.0

Soil	pH	Absorbance at 400nm	% Humic Acid Adsorbed
Ss Na^+	3.5	2.26	71 ± 15
Ss Ca^{2+}	3.5	1.17	85 ± 15
Ss	3.5	1.95	75 ± 10
Ss Na^+	7.0	7.55	3 ± 1
Ss Ca^{2+}	7.0	7.25	7 ± 1
Ss	7.0	7.18	8 ± 1
Sa Na^+	3.5	1.71	78 ± 10
Sa Ca^+	3.5	0.47	94 ± 10
Sa	3.5	0.31	96 ± 10
Sa Na^+	7.0	7.41	5 ± 1
Sa Ca^{2+}	7.0	7.33	6 ± 1
Sa	7.0	7.18	8 ± 1
Control	3.5	7.78	
Control	7.8	7.80	

cannot occur and so a decrease in the humic acid concentration in solution indicates adsorption has taken place. The control in which sodium humate was adjusted to pH 3.5 shows that this concentration of hydrogen ions does not precipitate the humic acid.

Therefore in the adsorption work carried out in further studies, sodium saturated soil and sodium saturated humic acid adjusted to pH 3.5 were used.

The adsorption of humic acid by natural soil (Kilmarnock arable (Ka) and Ragdale arable (Ra)) at pH 3.5 and 7.0, was also examined. The results for the Kilmarnock soil were 72% humic acid adsorbed at pH 3.5 and 3% adsorbed at pH 7.0. The Ragdale soil adsorbed all the humic acid at pH 3.5 and 8% at pH 7.0. The

particle size analysis of Ka and Ra showed that they contain 26% and 35% clay respectively compared to Sa which has 33% clay. The results show that the soil with the largest clay content (Ra) adsorbs the most humic acid (100%), and the soil with the lowest clay content (Ka) adsorbs least (72%), Sa being intermediate. This again indicates that it is the clay fraction which is adsorbing the humic acid.

The humic acid extracted with 0.5M NaoH from Stirling permanent pasture and Kilmarnock permanent pasture was also adsorbed onto Sa and Ss. The values for the amount of humic acid adsorbed were similar in both cases to those when humic acid extracted from a Fen peat was used. However, the readings for the absorbance of a 2mg/ml solution at pH 7.0 of each extract were different; the values were: Peat humic acid, 7.80; Sp humic acid, 5.80; Kp humic acid, 4.65. This indicates that the different humic acids have different extinction coefficients.

In these adsorption experiments 1M hydrochloric acid was used to adjust the pH from 7.0 to 3.5. Although this is a very satisfactory method for adjusting the pH accurately, chloride ions are introduced into the adsorption system. As an alternative, hydrogen saturated Dowex was added to increase the hydrogen ion concentration and give a pH of 3.5 without increasing the ionic strength. When the Dowex was allowed to mix intimately with the soil and humic acid, the values for the amount of humic acid adsorbed were similar to those using 1M hydrochloric acid. However, in a large scale experiment in which the stability of the soil aggregates was to be measured, it is necessary for the Dowex resin to be removed. The difficulties involved in removing the Dowex rendered this procedure impractical. The

process of physically extracting the Dowex resin with a sieve would increase the volume of liquid to be freeze-dried. As freeze- drying of the samples was the limiting step in the preparation of reformed soil aggregates by the adsorption of organic compounds, this procedure was rejected.

A second method using hydrogen saturated Dowex resin contained in dialysis tubing was also tried. This procedure did not decrease the pH of the soil/humic acid solution substantially when added. A time study monitoring the pH showed that whereas Dowex mixed intimately reduced the pH within five minutes, a similar amount of Dowex added in dialysis tubing only gave a decrease of 0.5 pH unit in 3 hours. It is possible that hydrogen ions are exchanged for the sodium ions on the humic acid, and because the hydrogen ion concentration in solution is not altered the pH of the solution will not change. Alternatively the ion-exchange process is greatly slowed down by the dialysis tubing.

From these experiments it was decided to use 1M hydrochloric acid to reduce the pH of the humic acid/soil mixture to 3.5 in large scale adsorption studies. The amount of humic acid added per gram of soil was kept at the same level (2%) for the large scale adsorptions as that used in the test-tube experiments.

4.2.3. Preparation of Reformed Soil Aggregates

Before additions of materials could be made to soils to see if there was an improvement in aggregate stability, a procedure had to be established that could be used for all the experiments to be carried out. The first priority was to find a method by which natural soil, after grinding to pass through a 0.5mm sieve, could be reformed into aggregates that approximated to those found in the

field, with respect to chemical and physical properties; mainly aggregate stability.

Four methods were described in section 3.2.2.3 that were used in attempts to reform soil aggregates from soil that had been ground to pass a 0.5mm sieve. It was found that aggregates prepared by cutting a soil pad with a scalpel and then dried at 50°C produced no stable aggregates when wet-sieved. Such observations were also made by Griffiths and Jones (1965), who prepared artificial aggregates by a similar procedure. They forced a soil paste from a hypodermic syringe into 15cm lengths, and after being allowed to dry slightly these were cut into 2mm portions. Using the water-drop method the aggregates were shown to be unstable, disintegrating after impact with five water drops.

The freezing and thawing and/or wetting and drying cycles employed also failed to produce stable soil aggregates when wet-sieved. Conflicting reports have been made concerning the effect of climatic factors on the formation and destruction of soil aggregates. Many workers (Rost and Rowles, 1941; Slater and Hopp, 1949; Chepil, 1954) found that freezing and thawing did not influence aggregate stability, but the action of frost on the soil did cause breakdown of aggregates into smaller entities. This process does not occur in every soil type and is dependent on many variables, such as the rate of freezing, the moisture content and clay content of the soil. Several workers (Bouyoucos, 1924; McHenry and Russell, 1944) reported that wetting and drying of the soil caused aggregate formation. On the other hand, Rost and Rowles (1941) and Willis (1955) found that this treatment did not increase the amount of stable soil aggregates.

Although freezing and thawing and/or wetting and drying have not been shown to be directly related to the stabilisation of soil aggregates, it is certain that these agencies play an important role in the formation process. Both of these processes cause movement of soil particles relative to each other and this constant reorientation should afford better opportunities for suitable conditions for aggregation to occur.

4.2.4. Reformation of Soil Aggregates using Additions of Organic Material

4.2.4.1. Incubation Experiments using 5% Additions of Glucose and other Organic Materials

Table 10 gives the mean weight diameter values for reformed soil aggregates of soils Sp, Sa and Ss after being incubated with organic material for 7, 14 and 21 days. The results show that after an incubation period of 1 week a 5% addition of glucose to Sp gave soil aggregates with a stability approaching that of natural aggregates. However, over the next two weeks the stability of the reformed aggregates gradually declined. After 7 days incubation a 5% glucose addition had made very little improvement to the stability of Sa or Ss. During the following two weeks the Sa attained a MWD of 102, almost the value for natural Sa aggregates, but the stability of aggregates from Ss did not change.

Addition of 5% glucose + 5% starch gave MWD values for Sa and Ss of 130 and 85 respectively, after 7 days incubation. Both of these values are higher than the MWD of the natural soil aggregates. A 5% glucose + 5% starch addition to Sp gave aggregates with a stability approaching that of natural aggregates.

These results show that organic amendments are capable of

Table 10 The Mean Weight Diameter Values of Soil Incubated with Additions of Glucose and Starch

Soil	Addition	Incubation time (days)			Variability	Natural Aggregates
		7	14	21		
Sp	5% glucose	200	160	83	± 15	223
Sa		30	59	102	± 10	118
Ss		25	25	27	± 1	37
Sp	5% glucose +5% starch	220	158	130	± 10	223
Sa		130	63	47	± 10	118
Ss		85	45	30	± 10	37

bringing about the formation of stable soil aggregates. The fact that glucose + starch gave Sa and Ss aggregates that were relatively stable after 7 days, whereas glucose alone had very little effect, indicates that the way in which aggregates were stabilised was not the same in both incubations. Glucose added to the soil would be utilised quickly by microorganisms, for metabolic processes and in some instances for the production of extracellular polysaccharides. Such polysaccharides could then be involved in the formation and stabilisation of soil aggregates. The fact that Ss had no stable aggregates greater than 0.5mm, suggests that some other factor as well as the polysaccharide is required for the stabilisation of aggregates. The indigenous organic matter or nitrogen that Ss contains are very low compared with those of Sp and Sa. It may be that the extracellular polysaccharide stabilises aggregates smaller than 0.5mm in Ss, but the quantity produced is not sufficient to reform larger aggregates.

When starch and glucose were added together both compounds would be utilised by microorganisms, but in addition the starch could be capable of cementing soil particles together to form stable aggregates. This could account for the aggregates of Sa and Ss being stable after 7 days incubation when starch was added. However the effect is not permanent, the stability of the aggregates declining over the following two weeks.

Additions of coarse organic material, cotton and hair at 5% level with glucose to Sp, Sa and Ss. The coarse organic material or "light fraction" was separated from a permanent pasture soil by flotation on water. The reformed aggregates removed from these incubations were found to be completely unstable (MWD = 25) after a period of 7 days and also after 14 days. The fact that no stable aggregates were obtained when an addition of coarse organic material was made to soil, indicates that this organic matter fraction is not involved in aggregate formation and stabilisation. Hence plant roots as such are not stabilising agencies themselves although their activities (e.g. mycorhizal activity and drying out of soil in the rhizosphere) might be.

The cotton and human hair added were chopped into very small lengths (2-5mm) before being mixed into the soil. It was thought that if aggregation was a physical process these strands would act as focal points for the process to occur. It has been argued that roots bring about aggregation of soil particles in this way. The results obtained from the incubations show that neither material was associated with stable aggregates.

Examination of the aggregates present in the foil trays, when in a dry state prior to rewetting with distilled water, revealed that they were very hard as though cemented together. The

aggregates of Ss showed this property more than those of Sa, and these more than Sp. As the incubation proceded it was noted that the aggregates became more friable, breaking down more readily into smaller entities. This behaviour was evident with Sp after a few days, Sa and Ss after 1-2 weeks.

The results presented in Table 10 are the mean of four replicates. The aggregate stability values varied considerably for a given treatment. For example when glucose and starch were added together the mean weight diameter value had a standard deviation of $\pm$ 10. One reason for this large variation was thought to be the problem of maintaining uniform conditions. Although the trays were re-moistened with a weight of water equal to that lost over the previous two days, replicate samples were certain to have different conditions. Griffiths and Jones (1965) also obtained data for aggregate stability, after organic amendments, with considerable variation amongst replicates in their incubation studies.

Despite these problems the results do show that glucose amendment is capable of promoting the formation of stable soil aggregates after a period of incubation. If refinements are made to the incubation technique to reduce the variability of the results, the addition of glucose to reform soil aggregates could prove to be the basis of further experiments.

4.2.4.2. Incubation of Soil with a Specific Microorganism

Griffiths and Jones (1965) made several amendments to soil and measured their effect on the stability of the reformed aggregates by the water-drop method. An addition of fungal mycellium followed by incubation produced aggregates with higher stability than did an incubation with glucose. As a result of this work a natural soil

microorganism, capable of producing extracellular polysaccharide material, was added to Sp, Sa, Ss and Ra. An azotobacter culture was selected and added to the soil in a glucose solution. The amount of glucose, added to provide a ready energy source for the microorganisms, was reduced from the 5g/100g soil used in the previous experiments to 2g/100g soil. Also conical flasks were used as containers so that the neck of the flask could be covered with tin foil to prevent other microorganisms from contaminating the samples.

The results for the stability of the reformed aggregates after 7 and 14 days incubation are given in Table 11. The aggregate stability values for the controls (soil + 2% glucose) are not significantly different from those of the samples containing the azotobacter inoculum. Therefore very little information was gained from this experiment concerning the effect of a soil microorganism producing natural soil polysaccharides in situ on the stability of soil aggregates. The main point to arise from this experiment was that under the conditions created a 2% glucose addition gave values for mean weight diameter that were higher than those obtained with 5% glucose in foil trays. (20mls of 10% glucose/100g 2%). The experiment was stopped after fourteen days because the microbial activity was so great that mycellia had grown and anaerobic conditions prevailed.

The fact that the aggregates from the controls were in general as stable as those from azotobacter inoculated flasks, indicates that the natural soil organisms are as good, if not better, at producing extracellular polysaccharide which can stabilise soil aggregates.

Table 11 The Mean Weight Diameter Values of Aggregates Reformed by the Addition of an Azotobacter Inoculum in a 10% glucose solution

Soil	Incubation period (days)	
	7	14
Sp	206 ± 1	215 ± 5
Sp control*	207	214
Sa	180 ± 30	222 ± 5
Sa control*	204	216
Ss	93 ± 10	173 ± 20
Ss control*	117	75
Ra	85 ± 30	189 ± 15
Ra control*	96	153

*Controls - only 2% glucose added.

4.2.4.3. Incubation Experiments Using 0.5% Glucose Additions

Although a method was required that would reform stable soil aggregates, it was not desirable that the method should give aggregates with maximum stability, as measured by wet-sieving. Experimentally, the aim was to obtain intermediate increases in aggregate stability following incubation with a glucose addition, so that differences between treatments could be detected. This would also permit the effect of a second organic amendment on the stability of the reformed aggregates to be studied. Therefore in the following experiments the level of glucose added was reduced to 0.5%.

Long term experiment. The mean weight diameter values of the 2.0-2.8mm soil aggregates wet-sieved after 1,3,5,8 and 12 weeks are shown in Table 12. The values obtained indicate that a 0.5% addition of glucose is creating conditions in the soil that lead to the formation of stable soil aggregates. The stability of reformed aggregates

Table 12 The Mean Weight Diameter Values for Reformed Aggregates of Sp, Sa and Ss Incubated with a 0.5% Addition of Glucose

Soil	Incubation period (weeks)					Natural Aggregates
	1	3	5	8	12	
Sp	204 ± 6	182 ± 2	172 ± 5	128 ± 2	90 ± 2	223
Sa	118 ± 3	132 ± 2	124 ± 1	100 ± 1	62 ± 2	118
Ss	63 ± 4	75 ± 5	49 ± 1	33 ± 1	30 ± 1	37

from Sp reaches a maximum in the first week of the incubation and then declines gradually over the next eleven weeks. The aggregates from Sa and Ss attain their maximum stability by the third week and then decline. The values for Ss indicate the absence of stable aggregates by the twelfth week.

The stability of the reformed aggregates is transient and the glucose is not capable of producing long term stabilisation of soil aggregates. It appears that the glucose is acting as an energy source for the microbial population in the soil. The microorganisms utilise some glucose for metabollic processes and reproduction, but also for the production of extracellular polysaccharides. Presumably it is this polysaccharide material which brings about the formation and stabilisation of soil aggregates. When all the glucose has been respired or degraded the microorganisms will then utilise the newly formed polysaccharide material; as this happens the stability of the soil aggregates declines. In a natural situation there must be some other factor present which is capable of stabilising the structure formed and giving rise to long-term aggregate stability.

Comparing the results for Sa and Ss with those from the

previous two experiments, a 0.5% addition of glucose gave higher stability of reformed aggregates than a 5% addition (Table 10), but lower values than a 2% addition (Table 11). The fact that a 0.5% addition produces aggregates which have a higher stability than a 5% addition, shows that the conditions prevailing in an incubation kept continuously moist, are much more conducive to reforming stable soil aggregation than an incubation with cycles of wetting and drying.

One explanation could be that the microorganisms which are responsible for stabilising aggregates, find continuously moist conditions more favourable for the production of extracellular polysaccharide. However, in such an incubation care must be taken to avoid anaerobic conditions.

The use of the low level glucose addition has two major advantages. The fact that it gives moderate enhancement of aggregate stability allows the observation of an additional effect of a second amendment. Also the temporary nature of the glucose activity similarly aids the detection of longer-term effects resulting from the addition of other compounds.

Reproducibility of MWD determinations. An experiment was carried out to determine how variable the MWD results were from replicate additions. The mean weight diameter values of aggregates for seven samples of Ss and three samples of Sa were determined over a period of three weeks. In the previous experiment the reformed aggregates had reached their highest stability value in this time. The results are presented in Table 13.

The mean weight diameter values obtained for reformed aggregates from replicate incubations show that the results for Sa had

a smaller standard deviation than those of Ss.

Table 13 The Mean Weight Diameter Values of Sa and Ss Incubated for Three Weeks with a 0.5% Glucose Addition

Sample	Incubation period (weeks)		
	1	2	3
Sa control	27	29	28
Sa + glucose	118	127	121
Sa + glucose	124	126	118
Sa + glucose	110	130	125
Mean	117	128	121
Standard Deviation	± 7	± 2	± 3
Ss control	25	27	26
Ss + glucose	51	59	65
Ss + glucose	65	77	78
Ss + glucose	80	90	75
Ss + glucose	55	62	64
Ss + glucose	67	75	71
Ss + glucose	69	86	80
Ss + glucose	53	66	64
Mean	63	74	71
Standard Deviation	± 10	± 12	± 7

The Sa samples have a mean aggregate stability of 127 ± 2 after 2 weeks incubation and a mean of 121 ± 3 after 3 weeks. The percentage error of these results is very small. The results of the Ss are more variable, e.g. after 2 weeks incubation the mean aggregate stability was 74 ± 12.

These values reflect what was generally found in incubation studies; i.e. that the higher the mean of the aggregate stability values the lower the standard deviation. This was also found to be the case when natural aggregates were wet-sieved. Considering that an incubation experiment followed by wet-sieving has so many

variables (e.g. moisture content, microbial population, type of microorganism, etc.) the results obtained for the Stirling subsoil are reasonable. However, a certain amount of care should be exercised when interpreting such results.

Incubation with a wetting and drying cycle. The incubations carried out up to date using a 0.5% glucose addition have been kept continuously moist. It was concluded from the experiments using a 5% glucose addition, in which the soil was re-moistened every second day, that the wetting and drying of the soil was not beneficial for reforming stable aggregates. An experiment (section 3.2.2.9(c)) was designed to test if a wetting and drying cycle would give an increase in the stability of aggregates at the lower value of glucose amendment.

The mean weight diameter values of the reformed aggregates after 1 and 2 weeks are presented in Table 14. Comparing the aggregate stability values after 1 week with those obtained in the long-term incubation (Table 12) it can be seen that Sp and Ss have lower values after a wetting/drying cycle, but those of Sa are similar in the two methods. Although this indicates that wetting and drying

Table 14 The Mean Weight Diameter Values for Reformed Aggregates of Sp, Sa and Ss after Incubation with 0.5% glucose with a Wetting and Drying cycle

Soil	Incubation period (weeks)	
	1	2
Sp	160 ± 1	90 ± 2
Sa	118 ± 9	126 ± 5
Ss	43 ± 8	35 ± 7

once did not create conditions which could have given an increase in aggregate stability, it cannot be said that the process was detrimental to the stability of the aggregates reformed by the addition of glucose.

In Section 4.2.2. the effect of wetting and drying alone on aggregate stability was discussed. This experiment reinforces the statement that the process did not stabilise aggregates, but could be important moving particles relative to one another, thereby giving a greater chance of conditions being suitable for aggregate formation and stabilisation.

Incubation with a split addition of glucose. This experiment (Section 3.2.2.9(c)) was carried out to see if addition of the glucose at weekly intervals increased the stability of the reformed soil aggregates. The mean weight diameter value of Sp (Table 15) was much lower than those previously obtained for a 0.5% addition of glucose. However, the MWD values of Sa and Ss were similar to those obtained for a single glucose addition, either kept continuously moist or with a drying cycle.

Table 15 The Mean Weight Diameter Values of Aggregates Reformed after Incubation with a Split Addition of Glucose (0.25g added initially and 0.25g added after 1 week)

Soil	Incubation period 2 weeks
Sp	92 ± 12
Sa	97 ± 8
Ss	45 ± 10

Conclusions. Three incubation experiments, namely 0.5% glucose kept continuously moist, 0.5% glucose with a wetting and drying cycle and 0.5% glucose in two additions, were carried out to compare the stability of the reformed aggregates. The variability of the aggregate stability values obtained in the three studies were similar, but the continuously moist incubation gave higher values for the stability of Sp and Ss. For this reason and also because a continuously moist incubation eliminated the variables involved in a drying and wetting procedure or a second glucose addition, it was decided to use a moist incubation in all further experiments to reform soil aggregates.

4.2.5. Incubation Experiment in which the Production of Carbon Dioxide was Monitored

In Section 4.2.4. it was suggested that the microorganisms were almost certain to utilise the 0.5g of glucose added/100g soil in a two to three week incubation. This theory was tested by incubating 0.5g glucose with 10g of Sp, Sa and Ss in separate 500ml conical flasks sealed with a suba-seal. By quantitatively determining the level of carbon dioxide present in the flasks using a gas chromatograph, the amount of glucose respired was calculated (Table 16).

The production of carbon dioxide in the flasks showed that Sp has a very high microorganism respiration rate in the first and second week compared with Sa and Ss. However, by the third week the amount of carbon dioxide present in Sa and Ss was higher than that of Sp, although the cumulative volume of carbon dioxide released was much less. The controls, which did not have glucose added, released some carbon dioxide; Sp producing a total cumulative volume of 24ml, more than twice that produced by Sa or Ss.

If the volume of carbon dioxide is regarded as a measure of

the microbial activity within the soil, then these results reinforce the observations made previously concerning incubations with glucose. It would appear that following an addition of glucose to Sp there is a rapid increase in the microbial numbers, with a corresponding rise in activity, which subsequently declines as the glucose is metabolised. The stability of the aggregates reformed is high when the microbial activity is great and decreases as the activity declines. Similarly in Sa and Ss, as the microbial activity rises to a maximum in the third week, so does the stability of the soil aggregates. This appears to be very good evidence for suggesting that the processes involved in the formation and short-term stabilisation of soil aggregates are dependent on the activity of soil microorganisms.

The figures for the total amount of carbon dioxide produced can be converted to a weight, and then the amount of glucose respired can be determined. The values for the amount of glucose respired are Sp 100%, Sa 50% and Ss 35%. This glucose is utilised for metabolic processes and in some microorganisms for the production of extracellular polysaccharides, which would then be capable of bringing about the short-term stabilisation of reformed aggregates that has been measured.

From this experiment it seems almost certain that when a 0.5% glucose addition is made (one tenth that used in this incubation), the glucose will be respired within two to three weeks. Therefore, if a second amendment was made to an incubation with added glucose, any effect greater than that of glucose alone could be attributed to the second amendment and not to residual glucose.

Table 16 The Carbon Dioxide Produced and the Percentage of the Addition Respired in Incubations, With and Without Glucose

Sample	No. of ml CO_2 produced			Cumulative Total	% Addition Respired
	Week 1	Week 2	Week 3		
Sp	185 ± 4	143 ± 2	69 ± 1	397	100
Sp control	10	5	9	24	
Sa	38 ± 1	34 ± 1	108 ± 1	180	50
Sa control	5	3	2	10	
Ss	10 ± 1	17 ± 1	105 ± 1	132	35
Ss control	2	2	6	10	

Calculation

$$\% \text{ glucose respired} = \frac{\text{Ml } CO_2 \text{ produced} \times \frac{273}{303} \times \frac{44}{22400} \times 100}{0.733}$$

where 1ml CO_2 is equivalent to $\frac{44}{22400}$ g

and $\frac{273}{303}$ is the correction for temperature.

Calculation of the total possible CO_2 production

$$6O_2 + C_6H_{12}O_6 \rightarrow 6\,H_2O + 6\,CO_2$$

$$180 \rightarrow 264$$

$$\therefore \quad 0.5 \rightarrow \frac{264}{2 \times 180}$$

$$= 0.733\text{g}$$

4.2.6. Reformation of Aggregates by the Addition of Polysaccharide

4.2.6.1. Experiment to Find the Level of Polysaccharide Necessary to Reform Stable Soil Aggregates

The aggregates produced following polysaccharide additions were very hard and difficult to break down if allowed to dry out completely before the aggregates were collected. Table 17 gives the

mean weight diameter values for various levels of microbial alginate and Xanthan gum additions to Ss. In general, the Xanthan gum tended to stabilise soil aggregates more effectively than microbial alginate at a given level of polysaccharide addition. The results show that the stability of the aggregates increased as the polysaccharide addition was increased from 0.05% to 0.5%; at the highest level the mean weight diameter was attaining high values.

The polysaccharide additions bring about the stabilisation of reformed aggregates in less than 24 hours. This indicates that microorganisms are not involved in the stabilisation process, in contrast to when glucose additions were made. Therefore, the speed of action of the polysaccharide material suggests, that stabilisation occurs either through adsorption or by "gluing" of soil particles into aggregates. The fact that the polysaccharides have very high molecular weights ($\sim 2 \times 10^6$) is consistent with both of these concepts.

Table 17 The Mean Weight Diameter Values of Ss Aggregates Reformed by the Addition of Various Levels of Polysaccharide

% polysaccharide added	Microbial Alginate	Xanthan Gum
0	25	27
0.05	26	49
0.75	39	81
0.10	41	97
0.25	172	164
0.50	185	208

4.2.6.2. Addition of Polysaccharide to Natural Aggregates

As an extension of the studies on the effect of polysaccharide additions, it was decided to make additions to samples of unstable natural aggregates (Section 3.2.2.9(d)). From the results in the previous experiment it was decided that the polysaccharide should be added at the 0.2% level. This was chosen because it was thought that aggregates with intermediate stability would be formed at this level of addition.

The aggregates with the polysaccharide additions were much more stable than the natural soil aggregates for the four soils used (see Table 18). The stability of Ss, Ra and Sx aggregates plus polysaccharide was at least double that of the natural aggregates. The aggregates of Sa had mean weight diameter values of over 200; this indicates that a large proportion of the aggregates did not disintegrate at all.

Table 18 The Mean Weight Diameter Values of Natural Soil Aggregates after a 0.2% Addition of Polysaccharide

Soil	Microbial Alginate	Xanthan Gum	Natural Aggregates
Sa	230 ± 2	211 ± 2	118
Ss	191 ± 2	103 ± 3	37
Ra	184 ± 2	189 ± 2	60
Sx	154 ± 3	161 ± 3	74

The polysaccharides, although sprayed onto the aggregates as an atomised solution, would probably not be able to penetrate into the aggregates. Not only their high molecular weight, but also the viscous nature of the polysaccharide in solution would make penetration

difficult. This would suggest the stabilisation of soil aggregates brought about by polysaccharides is a gluing or cementation action. In this instance through the high molecular weight polysaccharides forming a surface layer or film on the exterior of the soil aggregates.

4.2.6.3. Incubation Study to Determine the Duration of the Stability of Soil Aggregates Reformed after the Addition of 0.2% Polysaccharide

The stability of Sp aggregates reformed with a microbial alginate addition (Table 19) was highest after one day and then declined slowly over the next two weeks, with a sudden decrease in stability in the third week. The Sa aggregates have a mean weight diameter value of 77 after one day, this subsequently rises gradually over the next two weeks to a value of 108 and then declines to a MWD of 69 at the end of the third week. Although the absolute stabilities are not the same, this is a similar situation to that when glucose was added to the soil (Table 12).

However, in the case of Xanthan gum, additions to both Sp and Sa had a high stability after one day, which steadily declined over the next three weeks. Mean weight diameter values are also shown in Table 19 for samples of reformed Sp and Sa aggregates without any addition. These figures show that finely ground Sp and Sa do not form stable aggregates when incubated without an amendment.

The values obtained in this experiment show that although polysaccharides are very good agents for reforming

stable soil aggregates, the effect is transient. This is because, like glucose, these polysaccharides are easily degraded by the indigenous microbial population.

4.2.7. Reformation of Soil Aggregates after the Physical Addition of Humic and Fulvic Acids

The term physical is applied to these additions to distinguish them from later experiments (Section 4.2.8.) in which humic and fulvic acids were adsorbed at pH 3.5. In the physical additions all the components had been adjusted to pH7, before freeze-drying prior to mixing.

4.2.7.1. Additions of Humic Acid and Glucose

Humic acid in the sodium form was added as a solid to sodium and calcium saturated soils of Kilmarnock arable (Ka), Stirling arable (Sa) and Stirling subsoil (Ss), and incubated with glucose. The mean weight diameter values obtained when the reformed soil aggregates from these additions were wet-sieved, are presented in Table 20. This Table also contains the results from additions in which calcium humate was added to sodium and calcium saturated soil.

Three different humic acids, which were extracted with 0.1M sodium pyrophosphate (section 3.2.2.1.), were used in this study. Humic acid extracted from Kilmarnock permanent pasture and from a Fenland peat were added to Kilmarnock arable; and humic acid extracted from Stirling permanent pasture and from a Fenland peat were added to Stirling arable and Stirling subsoil.

The minimum value of the mean weight diameter obtainable from a wet-sieving determination with the apparatus used here is 25. This value indicates that all the soil aggregates placed on the uppermost sieve disintegrated completely and passed through the bottom, 0.5mm sieve.

The results presented in Table 20 show that the sodium and calcium saturated soil (both with and without glucose addition to act as an energy source for microorganisms) had very low aggregate

Table 19 The Mean Weight Diameter Values for Aggregates Reformed by the Addition of 0.2% Polysaccharide in a 3 Week Incubation

Soil	Addition	Incubation period (days)			
		1	7	14	21
Sp	0.2% microbial alginate	196 ± 3	170 ± 4	165 ± 4	61 ± 3
Sa	0.2% microbial alginate	77 ± 5	85 ± 5	108 ± 3	69 ± 4
Sp	0.2% Xanthan gum	177 ± 3	148 ± 3	90 ± 4	45 ± 2
Sa	0.2% Xanthan gum	134 ± 4	115 ± 5	70 ± 3	49 ± 2
Sp	none	30	37	35	32
Sa	none	27	28	27	27

stability values. When a 0.5% addition to natural soil of Sa and Ss was made the results obtained after a 2 week incubation (Table 13) were 128 ± 2 and 74 ± 12 respectively. From these results it appears that saturating the soil with sodium or calcium ions changes the soil environment so that microorganisms cannot reform stable aggregates with extracellular polysaccharide. This result is not surprising for a soil saturated with sodium, since natural soils with a large amount of exchangeable sodium are known to be unstable. However, as calcium is the dominant exchangeable cation of Stirling arable (pH7.0) it would be expected that calcium saturated Sa and natural Sa would give similar results.

Additions of calcium humate to both sodium and calcium saturated samples of the three soils did not stimulate the reformation of stable soil aggregates. The mean weight diameter values ranged from 32 to 43. However, when sodium humate was added to sodium saturated Kilmarnock arable an improvement in aggregate stability was seen. The humic acid from Kilmarnock permanent pasture gave higher mean weight diameter values than humic acid from the Fenland peat, in the presence of a glucose addition. With a peat humic acid addition only, the MWD was 47 ± 4.

It appears that the humic acid addition is responsible for an improvement in the stability of reformed aggregates. The fact that this improvement is enhanced by the addition of a glucose inoculum, suggests that microorganisms are involved. The addition of glucose only to Ka Na^+ gave a MWD of 33 ± 2, indicating it is not the glucose alone which is responsible for the enhanced stability. The additions of sodium humate to Sa Na^+ gave a similar series of results. However, the mean weight diameter when humic acid from

Table 20 The Mean Weight Diameter Values Obtained after 2 Weeks Incubation of Physical Additions of Humic Acid and Glucose

Soil	Addition of humic acid	Addition of glucose	MWD (2 weeks)
100g $KaNa^+$	2g Na^+Kp(NaOH)	0.5g	128 ± 16
100g $KaNa^+$	2g Na^+Peat(NaOH)	0.5g	85 ± 6
100g $KaNa^+$	2g Na^+Peat(NaOH)	0	47 ± 4
100g $KaNa^+$	2g Ca^{2+}Kp(NaOH)	0.5g	38 ± 2
100g $KaNa^+$	None	0.5g	33 ± 2
100g $KaCa^{2+}$	2g Na^+Kp(NaOH)	0.5g	50 ± 5
100g $KaCa2^+$	2g Ca^{2+}Kp(NaOH)	0.5g	41 ± 2
100g $KaCa^{2+}$	None	0.5g	35 ± 2
100g $SaNa^+$	2g Na^+Sp(NaOH)	0.5g	59 ± 4
100g $SaNa^+$	2g Na^+Peat(NaOH)	0.5g	37 ± 2
100g $SaNa^+$	2g Na^+Peat(NaOH)	0	34 ± 5
100g $SaNa^+$	2g Ca^{2+}Sp(NaOH)	0.5g	41 ± 2
100g $SaNa^+$	None	0.5g	27 ± 1
100g $SaCa^{2+}$	2g Na^+Sp(NaOH)	0.5g	53 ± 4
100g $SaCa^{2+}$	2g Ca^{2+}Sp(NaOH)	0.5g	43 ± 3
100g $SaCa^{2+}$	None	0.5g	37 ± 2
100g $SsNa^+$	2g Na^+Sp(NaOH)	0.5g	34 ± 2
100g $SsNa^+$	2g Ca^{2+}Sp(NaOH)	0.5g	35 ± 4
100g $SsNa^+$	None	0.5g	28 ± 1
100g $SsNa^+$	None	0	26 ± 1
100g $SsCa^{2+}$	2g Na^+Sp(NaOH)	0.5g	37 ± 2
100g $SsCa^{2+}$	2g Ca^{2+}Sp(NaOH)	0.5g	32 ± 2
100g $SsCa^{2+}$	None	0.5g	29 ± 1
100g $SsCa^{2+}$	None	0	26 ± 1

Stirling permanent pasture and glucose were added, was 59 ± 4 (cf. 128 ± 16 for $KaNa^+$ and Na^+Kp (NaOH)). The values obtained for the addition of peat humic acid to $SaNa^+$, both with and without glucose, were lower than the respective additions to $KaNa^+$. The addition of sodium humate from Stirling permanent pasture gave no improvement in aggregate stability when added to $SsNa^+$.

The improvement in stability of the reformed aggregates when sodium humate is added to sodium soil could be due to adsorption of the humic acid. Although the humic acid is added as a solid, when the sample of soil plus humate is wetted, the humic material will dissolve and be capable of adsorbing onto the soil. The results in section 4.2.2. showed that 7% of the sodium humate added was adsorbed onto Sa at pH 7.0. This amount of humic acid adsorption may well account for the improvement in aggregate stability detected after incubation. However, in the test-tube experiments 50ml of humic acid solution was added to 5g of soil, whereas in the incubation the soil is in a moist state. Therefore the sodium humate will be in very close contact (possibly direct contact) with the soil particles, and under these conditions the amount of adsorption could be greater than 7%. Alternatively the pH of the components may decrease with time of contact and low moisture levels and thereby increase the amount of adsorption.

The fact that when calcium humate, which is insoluble and unlikely to adsorb, was added no improvement in aggregate stability was observed suggests that this could be the correct explanation. Also the low MWD values obtained when sodium humate was added to calcium saturated soil of Ka and Sa (50 ± 5 and 53 ± 4 respectively) could be attributed to a lack of adsorption.

It should be noted that no combination of additions to Stirling subsoil increased the MWD value of the reformed aggregates above 40. This indicates that, in general, a physical admixture of clay and humic material does not produce stabilisation of soil aggregates. Also, a possible reason for Sa having a higher MWD for a given addition, could be due to the organic material which is already present on the clay particles.

4.2.7.2. Additions of Humic Acid and Polysaccharide

A second set of physical additions were carried out, but this time using a [illegible] polysaccharide instead of glucose. The polysaccharide, a microbial alginate in the sodium form (pH 7.0), was added at the 0.2% level. The results obtained in section 4.2.6.1. showed that this level of addition was sufficient to reform stable aggregates from finely ground soil. Table 21 presents the results of the additions of humic acid and polysaccharide to natural soil of Ka, Sa, Ss and calcium saturated soil of Stirling arable. The humic acid used was in the sodium form (pH 7.0) and had been extracted from a Fenland peat.

The mean weight diameter values (Table 21) show that the addition of polysaccharide, followed by a 2 week incubation, gives rise to some stable soil aggregates. For each soil tested the improvement in aggregate stability is greater when sodium humate is added with the polysaccharide. This is a similar result to that obtained in the last experiment when sodium humate and glucose were added to sodium saturated soil of Ka.

The mean weight diameter values after 4 and 6 weeks incubation, for humic acid additions plus polysaccharide and polysaccharide alone, show a decline in the stability of the reformed

aggregates. A similar decline was previously observed after glucose additions and polysaccharide additions (sections 4.2.4.3. and 4.2.6.3. respectively), and was attributed to the degradation of these substances and their products by microorganisms. This decline

Table 21 The Mean Weight Diameter Values Obtained after 2,4 and 6 Weeks Incubation, of Physical Additions of Humic Acid and Polysaccharide

Soil	Addition of humic acid	Addition of polysaccharide	Incubation period (weeks)		
			2	4	6
200g Ka	4g Na^+Peat(NaOH)	0.4g	172 ± 4	167 ± 8	80 ± 6
200g Ka	None	0.4g	101 ± 11	98 ± 17	54 ± 1
200g Ka	None	0	35 ± 4	33 ± 1	31 ± 1
200g Sa	4g Na^+Peat(NaOH)	0.4g	150 ± 2	153 ± 10	69 ± 10
200g Sa	None	0.4g	105 ± 1	72 ± 16	53 ± 10
200g Sa	None	0	27 ± 1	30 ± 1	26 ± 1
100g $SaCa^{2+}$	2g Na^+Peat(NaOH)	0.2g	203 ± 19	149 ± 5	
100g $SaCa^{2+}$	None	0.2g	49 ± 6	40 ± 11	
100g $SaCa^{2+}$	None	0	26 ± 1	28 ± 1	
100g Ss	2g Na^+Peat(NaOH)	0.2g	132 ± 10	37 ± 4	
100g Ss	None	0.2g	81 ± 17	41 ± 6	
100g Ss	None	0	26 ± 1	26 ± 1	

in stability of the reformed aggregates would suggest the major contribution towards the stabilisation of aggregates is from the polysaccharide addition, and an extra humic acid amendment enhances the improvement. The enhancement in stability of the reformed aggregates could be due to the adsorption of humic acid, as was suggested in the

previous experiment.

The transient nature of the improvement in aggregate stability indicates that the humic acid is not a major factor. This is based upon the knowledge that humic acid is relatively resistant to microbial attack and would not be expected to be degraded.

4.2.7.3. Additions of Fulvic Acid and Glucose

The method of extracting humic and fulvic acid used in this study (section 3.2.2.9.(f)) arbitrarily defines the fulvic acid as that portion of the extract which does not precipitate at pH 1. As well as containing the fulvic acid the supernatant also contains most of the soil polysaccharides extracted in the procedure. Determination of the total polysaccharide content of the fulvic acid extract by the phenol-concentrated sulphuric acid method revealed that it contained between 25-35% polysaccharide material.

It was decided to add the fulvic acid to the soil to see if the natural polysaccharide would promote the reformation of stable aggregates. This is also an extension of the previous study because the addition incorporates both polysaccharide and humic material. The fulvic acid added was a mixture (1:1 with respect to weight) of the sodium hydroxide extracts from Kilmarnock permanent pasture and Kilmarnock arable. The fulvic acid was in the sodium form (pH 7.0) and contained approximately 30% polysaccharide material. An addition of 1.5g fulvic acid was made because it would supply 0.5g of polysaccharide material (0.5g of glucose was added in previous experiments). The polysaccharide material could either act as a direct binding agent or indirectly as a food source for microorganisms to produce extracellular polysaccharide.

The results of the additions made to Stirling arable and Stirling subsoil are given in Table 22. A small increase in aggregate

stability was achieved with additions of fulvic acid, with and without glucose, for both soils. The value for addition of fulvic acid is greater than with fulvic acid and glucose. This is contrary to what was observed in the additions of humic acid and glucose. Also, when humic acid was added to Stirling arable the values were always greater than when it was added to Stirling subsoil. This might be expected since Sa has an aggregate stability value of 118

Table 22 The Mean Weight Diameter Values Obtained, after a 2 Week Incubation, for Physical Additions of Fulvic Acid to Sa and Ss

Soil	Addition of fulvic acid	Addition of glucose	MWD
100g Sa	1.5g	0.5g	49 ± 4
100g Sa	1.5g	0	62 ± 1
100g Sa	0	0	26 ± 1
100g Ss	1.5g	0.5g	42 ± 5
100g Ss	1.5g	0	86 ± 1
100g Ss	0	0	28 ± 2

for natural aggregates, whereas that of Ss is 37. But when fulvic acid was added alone, the reformed aggregates of Ss have a MWD value of 86 ± 1 whereas that of Sa was 62 ± 1. Insufficient fulvic acid was available to use larger volumes of soil, so that the stability of the aggregates could be monitored for a longer period.

To see if the polysaccharide material was being utilised by the microorganisms an experiment was set up to follow the production of carbon dioxide in the incubation (see section 3.2.2.9(e)). Four flasks were prepared, each with 10g of Sa and 0.15g fulvic acid or

0.5g glucose added as shown in Table 23. The Table also gives the number of millilitres of carbon dioxide produced in a given time and the percentage of the polysaccharide degraded, assuming it has the formula $C_6H_{12}O_6$. The fulvic acid used was a 1:1 mixture (w.r.t. weight) of the sodium hydroxide extracts from Kilmarnock permanent pasture and Kilmarnock arable. The percentage of material

Table 23 The Carbon Dioxide Produced and the Percentage of the Addition Respired in Incubations of Sa with Fulvic Acid and Glucose

Soil	Fulvic acid added	Glucose added	Volume of CO_2 produced (ml)			% addition respired
			Week 1	Week 2&3	Cumulative total	
10g Sa	.15g	.05g	44	22	66 ± 1	74
10g Sa	.15g	0	21	17	38 ± 1	72
10g Sa	0	.05g	36	5	41 ± 1	80
10g Sa	0	0	7	4	11 ± 1	

respired was calculated, assuming that 30% of the fulvic acid was polysaccharide. Therefore, the incubation of fulvic acid and glucose contained a total of 0.1g material which was susceptible to microbial attack. The results show that 74% of this material was respired in the incubation. The volume of CO_2 produced by Sa alone (11ml) was subtracted from the cumulative total for the volume of CO_2 produced in each incubation, to correct for the basic respiration of the microorganisms. In the circumstances this may represent an over-correction.

The incubations containing fulvic acid only showed that 72% of the polysaccharide material was respired. This indicates that the natural polysaccharides added to the soil are readily degraded by

the microorganisms. Also it shows that the polysaccharides must have been protected before they were extracted from the soil, and the extraction has removed that protection.

4.2.8. The Reformation of Soil Aggregates by the Adsorption of Humic and Fulvic Acid

The procedure for reforming soil aggregates after the adsorption of humic acid (3.2.2.10) did not permit the extent of adsorption to be monitored. Therefore it was necessary to conduct a series of experiments to study the adsorption of humic acid (if any) by the soils used (section 4.2.2.).

The following are important points which were made in section 4.2.2. :-

(a) Optimum pH for adsorption was 3.5, below this pH precipitation of humic acid occurred.

(b) Between 70-90% of the humic acid added was adsorbed at this pH in a sodium soil/sodium humate system.

(c) In a calcium soil/sodium humate system co-precipitation of humic acid could occur, which cannot be distinguished from adsorption.

The humic acid used in this study was extracted from Stirling permanent pasture and two peat soils. The sodium hydroxide extract of a Fenland peat was used for the initial eight adsorption experiments. In the later studies the pyrophosphate extracts from Stirling permanent pasture and the second peat soil (HA4, extracted from a basin peat) were used.

The adsorption was terminated, as stated in section 3.2.2.10., by the addition of calcium chloride, which saturates the system with calcium ions. Following the adsorption the small amount of humic

acid remaining in solution is precipitated and further adsorption prevented. Calcium hydroxide solution was added until the whole system was at pH 7, and then the soil/humic acid mixture was dialysed to remove the calcium and sodium chloride. After dialysis the sample was freeze-dried. This meant that the conditions for the added microorganisms during the incubation were as close as possible to those that would be encountered in a field situation.

The mean weight diameter values of the aggregates formed after the adsorption of humic acid and subsequent incubation with glucose are presented in Tables 24, 25 and 26. The first eight adsorptions (Table 24), in which sodium, ammonium and calcium saturated humic acid was adsorbed onto sodium and calcium saturated Ss, represent a preliminary study. In the course of these experiments

Table 24 The Mean Weight Diameter Values of Soil Aggregates Reformed after the Adsorption of Humic Acid onto Ss followed by a 2 Week Incubation

Soil	Humic acid added	Glucose added	MWD
100g $SsNa^{+}$	2g Na^{+}Peat(NaOH)	0.5g	145
100g $SsNa^{+}$	2g Na^{+}Peat(NaOH)	0.5g	137
100g $SsNa^{+}$	2g Na^{+}Peat(NaOH)	0.5g	142
100g $SsNa^{+}$	2g NH_4^{+}Peat(NaOH)	0.5g	176
100g $SsCa^{2+}$	2g Na^{+}Peat(NaOH)	0.5g	76
100g $SsCa^{2+}$	2g Na^{+}Peat(NaOH)	0.5g	64
100g $SsCa^{2+}$	2g Na^{+}Peat(NaOH)	0.5g	121
100g $SsNa^{+}$	2g Ca^{2+}Peat(NaOH)	0.5g	49
100g $SsNa^{+}$	None	0.5g	27
100g $SsNa^{+}$	None	0	26
100g $SsCa^{2+}$	None	0.5g	28
100g $SsCa^{2+}$	None	0	26

various points arose, concerning the techniques involved, which were corrected or improved upon for the later adsorptions. Therefore, although comparisons can be made within the group, it would not be correct to examine the MWD values in relation to later results.

Consider first the sodium soil ($SsNa^+$)/sodium humate (Na^+ Peat NaOH) systems in which adsorption of humic acid takes place. The MWD of the reformed aggregates range from 137-145 indicating that the procedure gave reproducible results. This is a considerable increase in aggregate stability over that of the natural Ss aggregates (37). The adsorption studies (section 4.2.2.) indicated that at least 70% of the humic acid was adsorbed.

When sodium humate was adsorbed onto calcium soil the MWD values, 76 and 64, were lower than those obtained in the all sodium system. The fact that these values are less than half of those obtained when sodium soil was used indicates that there is not the same amount of humic acid adsorbed on the calcium soil. This suggests that co-precipitation is taking place in this case; i.e. calcium ions from the soil are selectively exchanged for sodium ions on the humic acid molecules causing precipitation of the humic acid before adsorption can occur. The MWD for the attempted adsorption of calcium humate onto sodium subsoil was 49. This shows that calcium humate has very little effect on the stability of the reformed aggregates, and that adsorption probably did not occur.

The two adsorptions in which humic acid saturated with ammonium ions gave higher MWD values for the reformed aggregates than sodium humate. A possible explanation for these results is that the Ss will adsorb a greater amount of ammonium humate, or alternatively that the nitrogen added as the ammonium ion improved the

conditions for the microorganisms in the incubation.

Control incubations carried out both with and without glucose produced very few (if any) stable aggregates. Therefore, the improvements recorded when humic acid was adsorbed onto Ss must be due to the presence of the humic acid and not the glucose or its metabolic products.

The results of four adsorptions in which sodium saturated Sa was used are presented in Table 25. Sodium and calcium humate extracted from Stirling permanent pasture were added to sodium saturated soil. The aggregates reformed by the adsorption of sodium

Table 25 The Mean Weight Diameter Values of Soil Aggregates Reformed after the Adsorption of Humic Acid followed by a 2 week Incubation

Soil	Humic Acid adsorbed	Glucose added	MWD
100g $SaNa^+$	2g Na^+Sp (pyro)	0.5g	179
100g $SaNa^+$	2g Na^+Sp (pyro)	0	134
100g $SaNa^+$	2g $Ca^{2+}Sp$ (pyro)	0.5g	66
100g $SaNa^+$	2g $Ca^{2+}Sp$ (pyro)	0	40
100g $SaNa^+$	None	0.5g	35
100g $SaNa^+$	None	0	26
100g $SaCa^{2+}$	None	0.5g	38
100g $SaCa^{2+}$	None	0	27

humate gave MWD values of 179 with glucose and 134 without glucose. The improvement in structure obtained without an addition of glucose shows that humic acid alone is having a marked effect on both aggregate formation and stabilisation when it is properly adsorbed. The extra stability of the aggregates reformed after incubation with

a glucose addition would appear to be due to the microorganisms utilising the glucose, and producing extracellular polysaccharides which stabilise the reformed aggregates. This was the conclusion reached in earlier studies when aggregates were reformed with a glucose addition alone (Table 13).

Although it was shown in section 4.2.2. that calcium humate is not adsorbed by sodium soil, a large scale experiment using adsorption conditions was carried out so that a direct comparison could be made with the all sodium system. The MWD values obtained for the simulated adsorption of calcium humate onto $SaNa^+$ were 66 with glucose and 40 without glucose. Referring back to Table 20 it can be seen that the physical addition of calcium humate to $SaNa^+$ gave a MWD of 41 $\pm$ 2 with a glucose addition.

The results for the adsorption of three humic acids extracted with pyrophosphate onto Stirling subsoil are given in Table 26. The MWD values obtained when sodium humate from peat (175) HA4 (185) and Sp (179 and 184) were adsorbed on Ss with the addition of glucose are similar. The adsorption experiments (section 4.2.2.) showed that the amount of humic acid adsorbed by Ss was the same for humic acid extracted from Sp and peat. The results obtained here show that the three humic acid extracts are having a similar effect on the stability of the reformed aggregates.

Moreover, the stability monitored after a two week incubation had not declined when measured again after eight weeks. Therefore unlike the glucose (section 4.2.4.3.) and polysaccharide (section 4.2.6.3.) additions, in which the stability declined after 3 weeks, the humic acid was maintaining the stability of the reformed aggregates for a much longer period.

The MWD of the reformed Stirling subsoil aggregates (Table 26) is similar to the result of the adsorption of sodium humate to Stirling arable soil (Table 25). In some ways this is a surprising result, as natural Sa aggregates have a MWD of 118 while that of Ss was 37. Also when glucose or polysaccharide was added the reformed Sa aggregates had a higher aggregate stability than those of Ss. The Stirling arable and Stirling subsoil are formed from the same parent material and have the same clay content. Therefore it might

Table 26 The Mean Weight Diameter Values of Soil Aggregates Reformed after the Adsorption of Humic Acid followed by an 8 Week Incubation

Soil	Humic acid adsorbed	Glucose added	MWD	
			2 weeks	8 weeks
200g $SsNa^+$	4g Na^+ Peat(pyro)	1g	175	170
200g $SsNa^+$	4g Na^+ HA4 (pyro)	1g	185	173
200g $SsNa^+$	4g Na^+ Sp (pyro)	1g	184	182
200g $SsNa^+$	4g Na^+ Sp (pyro)	1g	179	176
200g $SsNa^+$	4g Ca^{2+} Sp (pyro)	1g	59	26
200g $SsNa^+$	4g Ca^{2+} HA4(pyro)	1g	51	28
200g $SsNa^+$	4g Na^+ Sp (pyro)	0	130	124

be expected that adsorption of humic acid onto the clay would give similar values for aggregate stability. The Sa soil does have some organic material present on the adsorption sites already, but the control experiments (Table 25) show that this does not have a significant effect on improving the stability of reformed aggregates.

An adsorption of sodium humate to Ss without added glucose, gave aggregates of lower stability than when an addition of glucose was made (Table 26). This was also seen to be the case for adsorptions onto Sa (Table 25). These results show that adsorption

of humic acid alone is capable of bringing about a degree of formation and stabilisation of soil aggregates. However, the stability of the reformed aggregates is greater when the adsorption is followed by an incubation with added glucose. Presumably the enhanced stability is due to the microorganisms producing extracellular polysaccharide, which then augments the effect that the humic acid adsorption is having.

The MWD values for the reformed aggregates after eight weeks incubation (Table 26) show that the enhancement in stability is still apparent. As the extracellular polysaccharide is degraded by the microorganisms, these results indicate that the humic acid is stabilising the aggregates reformed by the polysaccharide. An alternative might be that the extracellular polysaccharide is protected by the humic acid from microbial attack.

The attempted adsorption of calcium humate to Ss gave aggregate stability values of 59 and 51 for Ca^{2+}Sp(pyro) and Ca^{2+}HA4(pyro) respectively (Table 26). These MWD values are similar to those obtained previously (Table 25) when simulated adsorptions with calcium humate were carried out. However, incubating the samples for eight weeks showed that the MWD dropped to 26 and 28. This indicates that the slight improvement in aggregate stability observed when calcium humate was used is transient.

These experiments have shown that adsorption of humic acid followed by incubation with glucose produces reformed aggregates which are relatively stable (values of 180 cf natural Sp = 223). The stability of these aggregates is not transient, remaining at the same level for eight weeks. The stability of the reformed aggregates of Ss (175 - 185) shows that the adsorption of 2% sodium humate followed by incubation with 0.5% glucose has a remarkable ameliorating effect on aggregate structure.

There are also visual differences between the soils which have had humic acid adsorbed and the original soil (Plate 3). This photograph depicts Ss incubated with no amendments and incubated with 0.5% glucose after adsorption of 2% sodium humate. Comparing these two soils it can be seen that a 2% adsorption of humic acid has a profound effect on the soil colour; the humic acid imparting a dark brown colour to the light coloured natural Ss. Although it is not obvious from the photographs, the natural soil tended to contain larger aggregates than the more friable aggregates of the amended Ss.

The third soil shown in Plate 3 is Ss which had a simulated adsorption of 0.2% polyvinyl alcohol (PVA) followed by incubation with 0.5% glucose. The photograph shows that the PVA did not change the colour of the soil, but produced a well aggregated soil. The mean weight diameter value of the reformed soil aggregates was 231; indicating they are very stable. However, it was found that only 5% of the PVA was adsorbed by the soil, by measuring the organic material present in the supernatant solution. This shows that linear, flexible, uncharged polymers, such as PVA, are very effective in stabilising soil aggregates. The fact that 95% of the addition was not adsorbed suggests that the dominant stabilisation mechanism was cementation. But, this is more effective in stabilising soil aggregates than adsorption of humic acid. However, if a PVA stabilised soil aggregate was ruptured it would disintegrate completely. Disruption of an aggregate stabilised with humic acid would result in a number of smaller aggregates (two at least) which were stable themselves. In this case aggregation of the smaller particles could take place at some future date because the humic acid is still active.

Plate III

Stirling Subsoil which has had 2% Polyvinyl Alcohol, 2% Humic Acid and Nothing (Control) Adsorbed onto it and Incubated for 2 weeks

As an extension to the adsorption of whole humic acid extracts, samples of humic acid fractionated with respect to molecular weight were used. Originally it was hoped that a number of humic acid fractions could be obtained, using an Amicon ultrafiltration cell, and the effects of these fractions on the stability of reformed aggregates studied. A number of ultrafiltration membranes can be used to obtain molecular weight fractions at various intervals ranging from 5,000 - 300,000. However, when humic acid in the sodium form (pH 7.0) from the pyrophosphate extract of Stirling permanent pasture was fractionated, only a small proportion (5% on dry wt. basis) of the humic acid passed through the membrane partitioning at a nominal molecular weight of 300,000. Superficially, this would indicate that the pyrophosphate extract consists mainly of very high molecular weight polymers. It should also be noted that the pyrophosphate extract is a more oxidised extract than that obtained with sodium hydroxide.

Humic acid from a drained basin peat soil (HA4) was then fractionated, because it was thought that this would be more oxidised and have a larger proportion of lower molecular weight humic acid. This did prove to be the case, with 10% of the humic acid passing through the 300,000 membrane. However, this was still a surprisingly small percentage of low molecular weight humic acid. One explanation for these figures is that the partitioning molecular weight values quoted for the membranes, although correct for biological molecules such as proteins, are not correct for humic acid polymers. This is based upon the properties and shape of the humic acid polymer in solution (section 2.1.4.).

When a small quantity of 0.1M sodium chloride solution was added to the humic acid solution a much larger proportion passed through the 300,000 membrane. It is known that the presence of salt causes the open molecular structure of the randomly coiled polymer (Cameron et al, 1972) to change to a more globular structure (Flaig and Beutelspacher (1968). Therefore the molecular weight values of the fractions are not those quoted for the ultrafiltration membranes.

Sufficient humic acid from HA4 (pyrophosphate extract) passed through the 300,000 membrane to permit two molecular weight fractions of humic acid to be adsorbed onto the soil. The mean weight diameter values after a 2 week incubation period showed that the humic acid >300,000 from Sp and HA4 produced almost the same stability as the <300,000 fraction (Table 27). This stability persisted after eight weeks of incubation, indicating that both molecular weight fractions are capable of the long-term stabilisation of soil aggregates.

The MWD values obtained for the fractions (158 - 166) were slightly lower than those of the whole extracts (173 - 185), for Sp and HA4 humic acid. If one of the molecular weight fractions had given reformed aggregates with much greater stability than those obtained with whole humic acid extracts, then this would have indicated that this portion was the more active humic material concerned with stabilising soil aggregates. Since both molecular weight fractions have a similar effect, it would appear that molecular weight is not a major factor determining the ability of humic acid to reform stable aggregates. Although it may be that both fractions had sufficiently high molecular weight to stabilise the reformed aggregates effectively.

Table 27 The Mean Weight Diameter Values of Soil Aggregates Reformed After the Adsorption of Humic Acid Fractions followed by an 8 Week Incubation

Soil	Humic acid adsorbed	Glucose added	MWD	
			2	8
200g $SsNa^+$	4g Na^+Sp (pyro) >300,000*	0.5g	165	165
200g $SsNa^+$	4g Na^+HA4 (pyro) >300,000*	0.5g	166	164
200g $SsNa^+$	4g Na^+HA4 (pyro) <300,000*	0.5g	158	156

* The molecular weight values are nominal

Giovannini and Sequi (1976) found that when iron and aluminium were extracted from the soil, by acetylacetone in benzene, there was a decrease in the water stability of the soil aggregates. An adsorption was carried out using Stirling subsoil from which the iron and aluminium had been removed with sodium dithionite. This was a convenient method because it had the advantage of leaving the Stirling subsoil in the sodium saturated form. The results for the mean weight diameter of the aggregates reformed following this treatment are given in Table 28. These show that the stability of the reformed aggregates was the same for dithionite treated soil and for soil saturated with sodium. The removal of the iron and aluminium from the soil does not affect the stability of the reformed aggregates.

Table 29 presents the MWD values for aggregates reformed following the adsorption of fulvic acid (pyrophosphate extract) from Stirling permanent pasture and the Fenland peat. As the fulvic acid contains natural soil polysaccharides which act as an energy source for microorganisms (section 4.2.7.3.), no glucose was added. The

Table 28 The Mean Weight Diameter Values of Soil Aggregates Reformed after the Adsorption of Humic Acid onto Soil from from which Iron and Aluminium had been Removed

Soil	Humic acid adsorbed	MWD	
		2 weeks	8 weeks
200g Ss dith.	4g Na^+Sp (pyro)	148	130
200g $SsNa^+$	4g Na^+Sp (pyro)	139	126

MWD values for the adsorption of Sp fulvic acid and peat fulvic acid onto $SsNa^+$ were 72 and 58 respectively. These values are similar to those obtained when fulvic acid was physically added to the soil (section 4.2.7.3.), indicating that the fulvic acid was probably adsorbed after addition.

It was concluded from the adsorption of two humic acid fractions that molecular weight was not a major factor determining the ability of humic acid to reform stable aggregates. These results

Table 29 The Mean Weight Diameter Values of Soil Aggregates Reformed after the Adsorption of Fulvic Acid followed by a 2 Week Incubation

Soil	Fulvic acid adsorbed	MWD
200g $SsNa^+$	4g Na^+Sp (pyro)	72
200g $SsNa^+$	4g Na^+ Peat (pyro)	58

show that fulvic acid, a very low molecular weight fraction of humic acid, gave MWD values for reformed aggregates that were much lower than those obtained for whole humic acid extracts. This indicates that high molecular weight polymers are more efficient in reforming stable aggregates, and that there may be a molecular weight effect.

4.3. CONCLUSIONS

A survey of over one hundred predominantly heavier textured soils from the East of Scotland and England, showed that there was a highly significant correlation between total organic matter content and aggregate stability. Two soil organic matter components, namely polysaccharide and humic acid, were also found to have highly significant correlations with aggregate stability. These results indicate that both polysaccharide and humic acid are involved in the stabilisation of soil aggregates, but do not show that one of the organic matter fractions is more important than the other.

The incubation experiments carried out in the laboratory have shown that extracellular polysaccharide, produced by microorganisms from metabolisable organic material, is capable of reforming stable soil aggregates. However, the stability is only transient presumably because the polysaccharide material is degraded itself by the microbial population.

When humic acid is adsorbed onto the soil and incubated with glucose, stable aggregates are reformed which retain their stability over a period of eight weeks. This indicates that the humic acid is an organic matter component capable of bringing about the long-term stabilisation of soil aggregation.

Some evidence has been obtained in both the laboratory studies and in the survey work to suggest that the higher molecular weight humic acid molecules are more effective in stabilising soil aggregates than the more oxidised low molecular weight polymers. The theory that soil aggregates are stabilised by high molecular weigh humic acid polymers is consistent with the known properties of humic substances and clay colloids (sections 2.1. and 2.2. respectively).

A randomly coiled humic acid polymer, which has several side branches or strands, would be able to form attachments with a number of clay particles; through ion-exchange, cation bridging, sharing of adsorbed water, sharing of cations, etc. (see section 2.3.). The fact that humic acid molecules are capable of large volume changes means that they would be able to swell and shrink according to the moisture status of the soil. In addition, humic polymers are also capable of bonding to iron or aluminium oxides in the soil. This gives a soil system in which "strings" of humic acid are stabilising soil aggregates, by forming bonds between adjacent clay particles or adjacent clay and oxide particles.

The survey of agricultural soils shows that fields which are continuously cultivated, often have unstable soil aggregates. In these intensive arable farming systems there are no inputs of organic material and the total organic matter content gradually declines. The laboratory incubation studies have shown that an input of readily metabolisable organic material to the soil can create stable soil aggregates, even when the indigenous organic matter content is low. The aggregates reformed by the extracellular polysaccharide, which the microorganisms produce, can then be stabilised by the indigenous organic matter. Therefore, the results of these experiments indicate that although organic matter additions (such as farmyard manure, green manures and straw) do not increase the total organic matter content of a soil, they can nevertheless play an important role in promoting the formation and stabilisation of soil aggregates. From a soil structural viewpoint this would suggest that in an all-arable rotation, the organic matter residues of no economic importance should not be removed, either physically or by

burning, but should be returned to the soil.

4.3.1. Possible Areas for Further Study

In section 4.1.3. it was pointed out that the organic matter determinations included the coarse organic material, which is not adsorbed onto the soil, and is therefore of little use in the stabilisation of soil aggregates. If the inactive material was removed and then the carbon content, polysaccharide content and extractable humic acid determined, the values may be even better correlated with aggregate stability than those obtained in this study.

The regression line calculated from the results of mean weight diameter and total organic matter content indicated that a linear relationship existed, i.e. that the stability of natural soil aggregates is proportional to the total organic matter content. However, it was suggested that there might be a "critical" organic matter level (section 4.1.2.), and below this level there is not sufficient organic material to stabilise soil aggregates. A study of the field performance of the soils would give some idea of the "critical" organic matter level.

There were several experiments which were not carried out in section 4.2. because of the shortage of polysaccharide material. The yield of soil polysaccharide obtained in a soil extraction is in the order of 0.5%. This necessitates the extraction of very large quantities of soil, to obtain the amounts needed for large scale incubation experiments.

Experiments which could have been conducted are:-

1. The absorption of 2% humic acid onto finely ground soil followed by incubation with a 0.2% addition of soil polysaccharide material.

2. A comparison between the carbon dioxide production of 0.2% polysaccharide mixed with soil and 0.2% polysaccharide adsorbed by soil. This would show if the soil polysaccharide material is protected from microbial attack when adsorbed by the soil.

3. Monitoring the carbon dioxide produced when a 0.5% addition of glucose is incubated with soil that has had 2% humic acid adsorbed onto it. This would show if the extracellular polysaccharide is degraded by the microorganisms or remains in the soil protected from microbial attack by the humic acid. If the polysaccharide is degraded, this would be good evidence to suggest that polysaccharide material is responsible for the formation and initial stabilisation of soil aggregates, and humic acid stabilises the structure that is formed.

4. A more detailed look at the adsorption of humic acid alone. The fact that stable aggregates were reformed when humic acid adsorbed onto the soil was incubated alone, may suggest that the indigenous organic material is sufficient to create structure.

APPENDIX

Table A1

Soils Collected from the East of Scotland in 1975

Soil Series	Code Name	Farm	Grid Ref	Cultivation & Crop at Time of Sampling	Drainage Class
HUMBIE	Ha	MORHAM MAINS, HADDINGTON	NT 546707	Continuous cultivation - winter wheat	IMPERFECTLY DRAINED
	Hp	NORTHRIG, HADDINGTON	NT 550728	Permanent pasture	
KILMARNOCK	KKa	KILDUFF, HADDINGTON	NT 515772	Continuous cultivation - winter wheat	IMPERFECTLY DRAINED
	Kp	ATHELSTANEFORD MAINS HADDINGTON	NT 538769	Permanent pasture	
	Ka	ATHELSTANEFORD MAINS HADDINGTON	NT 537768	Continuous cultivation - barley	
DREGHORN	DRa	LUFFNESS MAINS, ABERLADY	NT 483797	Continuous cultivation - barley	FREELY DRAINED
PEFFER	PFa	LUFFNESS MAINS, ABERLADY	NT 489800	Continuous cultivation - cauliflowers	IMPERFECTLY DRAINED
BIEL	Bg	COVE FARM, COCKBURNSPATH	NT 783714	Garden, overgrown and undisturbed for few years	IMPERFECTLY DRAINED
	Ba	COVE FARM, COCKBURNSPATH	NT 783715	Continuous cultivation - barley	
	Bhr	COVE FARM, COCKBURNSPATH	NT 777716	Undisturbed ground in corner of field	
	Bnb	NORTH BELTON, DUNBAR	NT 634777	Continuous cultivation - barley	
STIRLING	Sa	ELLIOTHEAD FARM, BRIDGE OF EARN	NO 149181	Continuous cultivation - barley	POORLY DRAINED
	Sa	ELLIOTHEAD FARM, BRIDGE OF EARN	NO 149181	Continuous cultivation - the subsoil	
	Sp	OODENARD, BRIDGE OF EARN	NO 147182	Permanent pasture	
POW	Pa	MAINS OF DUN, MONTROSE	NO 667590	Continuous cultivation - barley	POORLY DRAINED
	Phr	MAINS OF DUN, MONTROSE	NO 668590	Undisturbed grass verge at roadside	
FORFAR	Fa	NORTH TARRY FARM ARBROATH	NO 646428	Continuous cultivation	FREELY DRAINED
	Fp	NORTH TARRY FARM ARBROATH	NO 644425	Permanent pasture	
LATERITE	Lt	BRAZIL, SOUTH AMERICA		Cerrado grassland	

Table A2

Soils Collected from England

SOIL SERIES	CODE NAME	FARM	GRID REF	CULTIVATION AND CROP AT TIME OF SAMPLING	DRAINAGE CLASS
RAGDALE	Ra	Campney Grange, Bardney	TF 154675	Continuous cultivation	POORLY DRAINED
	Rp1	Tupholme Hall, Bardney	TF 141694	Permanent pasture	
	Rp2	Lawfield Farm, Bardney	TF 142703	Permanent pasture	
	Rip	Tupholme Hall, Bardney	TF 138699	Improved permanent pasture - F.Y.M. added	
DENCHWORTH	Da		TF 085414	Continuous cultivation	POORLY DRAINED
	Dp		TF 079404	Permanent pasture	
BATCOMBE	Bf	Fosters Field, Rothamstead		Fallow	
BECCLES	Sx	Harwoods Field, Saxmundham		Continuous cultivation	IMPERFECTLY DRAINED
BENTLEY	P1	Admirals Farm, Gt Bentley	TM 119231	Continuous cultivation - turnips	
	P2	Bretts Hall, Tendring	TM 133232	Continuous cultivation - peas	
WIX	P3	Bretts Hall, Tendring	TM 131238	Continuous cultivation - spring wheat (surface erosion)	
LANDERMERE	P4	Landermere Hall, Thorpe-Le-Soken	TM 188232	Continuous cultivation - winter wheat	
ALTHORNE	P5	Landermere Hall, Thorpe-Le-Soken	TM 187229	Continuous cultivation - winter wheat	IMPERFECTLY DRAINED
	P5sub			Continuous cultivation - the subsoil	
RAGDALE	K3w	Mores Wood, Brentwood	TQ 561965	Coppiced hornbeam woodland	POORLY DRAINED
	K3a	Nr Mores Wood, Brentwood	TQ 561966	Continuous cultivation - winter wheat	
OAK	G1	Mattocks Farm, Gt Leighs	TL 702178	Continuous cultivation - wheat, peas, potatoes	POORLY DRAINED
HORNBEAM	G2	Ridley Hall, Terling	TL 757154	Permanent grassland - for dairy	
HAMBLE	G3	Terling Hall, Terling	TL 766132	Continuous cultivation - wheat, peas, potatoes	MODERATELY WELL DRAINED
BROCKHURST	BRa		SP 254583	Arable crops for past 7 years	POORLY DRAINED
	BRg		SP 358622	Grass for at least 10 years	
DENCHWORTH	DEa		SP 364568	Arable crops for 4 years	POORLY DRAINED
	DEg		SP 360571	Permanent grassland, reseeded 8 yrs ago	
WHIMPLE	WHa		SP 257583	Arable crops for past 7 years	MODERATELY WELL DRAINED
	WHg		SP 254580	Grass for at least 10 years	
WORCESTER	WOa		SP 345631	Rotation of 4 years cereal, 1 year grass for 12 years	IMPERFECTLY DRAINED
	WOg		SP 258577	Permanent grassland	

Table A3

Soils of the Kilmarnock Series

FARM	CODE NAME	GRID REF	CROP AT TIME OF SAMPLING	ROTATIONAL SYSTEM
AULDHAME NORTH BERWICK	A1	NT 593847	Grassland - 2nd year ley	Intensive diary with arable. Grassland is irrigated and 300 units N/annum + slurry applied.
	A2	NT 595847	Grassland - 3rd year ley	
	A3	NT 595845	Grassland - 4th year ley	
	A4	NT 594842	Grassland - 1st year ley	
	A5	NT 598843	Arable - cabbages	
	A6	NT 596843	Permanent grassland - reseeded 1969	
KILDUFF HADDINGTON	K7	NT 524776	Arable - continuous barley	3 years cereal 1 year potatoes
GILMERTON HOUSE HADDINGTON	GH8	NT 547778	Permanent pasture	Parkland
FERRYGATE NORTH BERWICK	FG9	NT 528842	Arable - winter wheat	arable/vegetables for 5 years and then a 1 year grass ley. 1 year in six farm yard manure applied to each field.
	FG10	NT 530842	Grassland - 1st year ley	
	FG11	NT 529846	Arable - barley	

Table A4

Soils of the Humbie Series

FARM	CODE NAME	GRID REF	CROP AT TIME OF SAMPLING	ROTATIONAL SYSTEM
LEASTON	L1	NT 489634	Arable - winter wheat	3 years cereal 2 years grass
	L2	NT 490634	Grassland - 2nd year ley	
	L3	NT 490635	Arable - winter wheat	
	L4	NT 481631	Grassland - 2nd year ley	
	L5	NT 481634	Arable - winter wheat	
HIGHLEAS	HL6	NT 468648	Grassland	2 years cereal 1 year potatoes 2 years grass
	HL7	NT 468647	Arable - barley	
	HL8	NT 470645	Potatoes	
WOODHEAD GIFFORD	WH9	NT 521668	Arable - barley	Barley has been grown continuously for 15 years on arable land.
	WH10	NT 519667	Permanent grassland	
	WH11	NT 514666	Arable - barley	
HUMBIE HOUSE	HH12	NT 471641	Permanent grassland	Parkland

Table A5

Soils of the Stirling Series

FARM	CODE NAME	GRID REF	CROP AT TIME OF SAMPLING	ROTATIONAL SYSTEM
MEGGOTLAND	ME1	NO 279268	Peas	Previous 7 yrs ley
	ME2	NO 281270	Peas	Continuous cultivation from '65
	ME3	NO 275270	Swedes	CC from 1969, previous mixed farming
	ME4	NO 274273	Barley	CC from 1970, previous mixed farming
POWGAVIE	P1	NO 287261	Permanent pasture for grazing	
	P2	NO 290259	Permanent pasture	
	P3	NO 283255	Permanent pasture under old orchard	
	P4	NO 289262	Cereals	Continuous cultivation
WEST MAINS OF INCHTURE	WM1	NO 280282	Cereals (+ potatoes)	7 yrs arable after mixed farming
	WM2	NO 282279	Potatoes (+ cereals)	7 yrs arable after mixed farming
BALGAY	BALG1	NO 269274	Barley	2 yrs cereals, previous p.p.
WATERBUTTS	WB1	NO 277260	Permanent pasture	Intensive dairy
	WB2	NO 275261	Permanent pasture reseeded 1975	Intensive dairy
	WB3	NO 277257	Grass ley	Grass until 2 yrs arable '73 and '74
WEST LEYS	WL3	NO 253241	Grass ley	Grass, 10 yrs arable, 2 yrs ley
	WL4	NO 258239	Cereals	Continuous cultivation from '65
	WL5	NO 260241	Cereals	Continuous cultivation from '65
	WL6	NO 260244	Cereals	Permanent pasture until1965, cereals
	WL7	NO 257244	Cereals	until 1972, ley 1973-75, cereals since .
	WL8	NO 259246	Cereals	Continuous cultivation from '65
	WL9	NO 263245	Cereals	Continuous cultivation from '65
BALCHALUM	BAL1	NO 236261	Grass	7 yrs ley, previously
	BAL2	NO 235259	Grass	rotationally cropped
	BAL3	NO 236259	Cereals	7 yrs cereals after mixed farming

Table A6

Soils of the Winton Series

FARM		CODE NAME	GRID REF	CROP AT TIME OF SAMPLING	ROTATIONAL SYSTEM
WOLFSTAR PENCAITLAND		W1	NT 416686	Arable - turnips	1 year grass 1 year roots 5 years cereals
		W2	NT 417684	Grass - 1st year ley, undersown barley	
		W3	NT 418684	Arable - barley	
		W4	NT 419687	Permanent grassland	
HODGES PENCAITLAND		HD5	NT 455718	Arable - barley	2 years grass 4 years cereal (occasional root crop)
		HD6	NT 458718	Grass - 2nd year ley	
		HD6S	NT 458718	Subsoil of HD6	
		HD7	NT 456718	Arable - barley	
BROWNHILLS ST. ANDREWS		BH8	NO 529149	Grassland - at least 8 years	
		BH9	NO 529153	Arable - peas	continuous arable
DENBRAE STRATHKINESS		DB10	NO 476150	Permanent grassland	not able to grow crops due to vermin
		DB11	NO 475150	Arable - barley	Continuous arable
		DB12	NO 446150	Arable - barley	
		DB13	NO 465150	Arable - barley	
EASTER GRANGEMUIR PITTENWEEN		C14	NO 543043	Grass - 1st year ley, undersown barley	2 years grass 3 years cereals
		C15	NO 544043	Arable - barley	
BUSH ESTATE	TOWER FIELD	TF16	NT 269646	Grassland - permanent	Intensive dairy
	PLOVERHALL	PH17	NT 259642	Arable	3 yrs arable 2yrs grass
	FOUNTAIN FIELD	FF18	NT 260638	Grassland	2 yrs arable 3yrs grass
	H.F.R.O.	HFRO19	NT 251634	Grassland - permanent	Grazing
	SOUTH ROAD	SR20	NT 259632	Arable	Continuous barley

Table A7

Results for Mean Weight Diameter and Determinations on Organic Matter and its Constituents for Soils Collected from the East of Scotland in 1975

SOIL	1	2	3	4	5	6	7	8
	Mean Weight Diameter M.W.D.	% Carbon	% Organic Matter	% Poly-saccharide	Optical Density of Humic Acid			
					0.1M $Na_2P_2O_7$	0.5M NaOH	Total of 5 & 6	0.5M NaOH only
Ha	132	2.11	3.7	0.68	1.09	1.22	2.31	1.38
Hp	225	3.24	5.6	1.50	2.32	2.75	5.07	3.45
KKa	98	1.80	3.1	0.55	1.42	1.94	3.36	1.97
Kp	219	4.80	8.4	2.05	2.55	4.10	6.65	5.27
Ka	148	2.30	4.0	0.95	1.59	1.63	3.22	2.61
DRa	71	2.19	3.8	0.53	1.73	1.68	3.41	2.11
PFa	53	1.72	3.0	0.65	0.81	0.87	1.68	0.70
Bg	215	4.59	8.0	1.68	2.50	4.80	7.30	5.85
Ba	82	1.81	3.2	0.58	1.36	1.77	3.13	1.80
Bhr	211	3.17	5.5	1.15	1.60	3.10	4.70	3.66
Bnb	72	2.93	5.1	0.93	1.35	1.53	2.88	1.67
Sa	118	2.08	3.6	1.08	2.61	1.93	4.54	2.60
Ss	37	0.28	0.5	0.05	1.54	1.00	2.54	1.52
Sp	223	5.47	9.5	3.50	4.58	3.31	7.89	6.53
Pa	54	1.99	3.5	1.05	1.04	0.91	1.95	1.27
Phr	215	4.55	7.9	2.50	2.05	3.92	5.97	4.62
Fa	140	1.54	2.7	0.53	1.35	1.12	2.47	1.76
Fp	166	3.31	5.8	1.18	2.43	2.00	4.43	3.60
Lt	185	2.47	4.3	2.25	2.91	2.05	4.96	3.60

Table A8 Results of Mean Weight Diameter and Determinations on Organic Matter and its Constituents for Soils from England

SOIL	1	2	3	4	5	6	7	8
	Mean Weight Diameter M.W.D.	% Carbon	% Organic Matter	% Poly-saccharide	Optical Density of Humic Acid			
					0.1M $Na_2P_2O_7$	0.5M NaOH	Total of 5 & 6	0.5M NaOH only
Ra	60	1.45	2.5	0.90	1.12	0.59	1.71	0.44
Rp1	166	3.80	6.6	2.50	2.35	1.98	4.33	1.73
Rp2	208	5.63	9.8	2.70	3.75	3.96	7.71	4.80
Rlp	176	5.25	9.1	2.10	3.55	2.60	6.15	3.18
Da	151	1.97	3.4	1.35	1.29	0.97	2.26	0.73
Dp	200	3.13	5.5	1.35	1.76	4.73	6.46	1.88
S x	79	1.03	1.8	0.50	0.79	0.43	1.22	0.30
Bf	74	1.10	1.9	0.45	0.76	0.49	1.25	0.38
P1	86	1.01	1.8	0.69	0.83	0.58	1.45	0.66
P2	99	0.96	1.7	0.70	0.86	0.78	1.64	0.65
P3	51	1.08	1.9	0.66	0.95	0.90	1.85	0.76
P4	91	1.47	2.6	0.73	1.04	0.62	1.66	0.52
P5	141	1.50	2.6	0.85	0.92	0.52	1.44	0.49
P5s	120	0.29	0.5	0.01	0.15	0.17	0.32	0.10
K3w	214	4.67	8.1	2.29	4.30	3.20	7.50	4.27
K3a	105	1.87	3.3	1.08	1.12	0.84	1.96	0 80
G1	95	1.49	2.6	0.85	0.88	0.53	1.41	0.50
G2	207	3.06	5.3	2.01	2.09	2.26	5.35	3.02
G3	35	1.10	1.9	0.73	0.89	0.55	1.44	0.56
BRa	120	1.27	2.2	0.90	0.75	0.88	1.63	0.88
BRg	193	2.50	4.4	1.50	1.65	1.69	3.34	1.13
DEa	111	3.96	6.9	2.89	2.59	0.52	3.11	2.53
DEg	210	4.55	7.9	2.94	4.10	0.70	4.80	4.90
WHa	116	1.32	2.3	0.80	0.87	0.96	1.83	1.05
WHg	169	2.38	4.1	1.49	1.08	1.46	2.54	1.44
WOa	94	2.33	6.1	1.29	1.00	1.12	2.12	1.03
WOg	213	5.37	9.3	2.95	1.62	2.47	4.09	2.06

Table A9 Results for Mean Weight Diameter and Determinations on Organic Matter Constituents and its Constituents for Soils of the Kilmarnock Series and the Humbie Series

SOIL	1	2	3	4	5	6	7	8
	Mean Weight Diameter M.W.D.	% Carbon	% Organic Matter	% Poly-saccharide	Optical Density of Humic Acid			
					0.1M $Na_2P_2O_7$	0.5M NaOH	Total of 5 & 6	0.5M NaOH only
A1	153	1.95	3.4	1.19	1.74	2.16	4.90	1.55
A2	146	2.13	3.7	1.37	2.25	2.16	4.41	2.07
A3	168	2.09	3.6	1.15	2.20	2.11	4.31	1.77
A4	151	1.91	3.3	0.80	1.90	2.03	3.93	1.65
A5	131	1.66	2.9	0.88	1.87	1.87	3.74	1.41
A6	189	2.49	4.3	1.51	2.33	2.52	4.85	2.89
K7	165	2.05	3.6	1.13	1.95	2.19	4.14	2.21
GH8	206	3.37	5.9	1.85	3.26	4.28	7.54	3.78
FG9	183	1.84	3.2	1.06	1.57	1.53	3.10	1.33
FG10	162	1.77	3.1	1.13	1.61	1.62	3.23	1.15
L1	144	2.07	3.6	1.24	1.84	1.83	3.67	2.17
L2	131	1.78	3.1	1.13	1.50	1.71	3.21	2.06
L3	161	1.95	3.4	0.99	2.08	1.76	3.84	2.70
L4	174	1.93	3.4	1.02	1.87	1.97	3.84	1.95
L5	181	1.79	3.1	1.01	1.84	1.56	3.40	2.20
HL6	101	1.72	3.0	1.03	1.28	1.63	2.91	1.46
HL7	125	1.36	2.4	0.82	1.15	1.40	2.55	1.37
HL8	156	1.59	2.8	0.94	1.36	1.61	2.97	1.53
WH9	116	1.91	3.3	1.13	1.74	1.83	3.57	2.11
WH10	203	2.32	4.0	1.65	1.50	1.90	3.40	2.19
WH11	144	1.86	3.2	1.00	1.79	1.51	3.30	2.24
HH12	217	3.32	5.8	2.11	3.00	2.48	5.48	4.22

Table A10

Results for Mean Weight Diameter and Determinations on Organic Matter and its Constituents for Soils of the Stirling Series

SOIL	1	2	3	4	5	6	7	8
	Mean Weight Diameter M.W.D.	% Carbon	% Organic Matter	% Poly-saccharide	Optical Density of Humic Acid			
					0.1M $Na_2P_2O_7$	0.5M NaOH	Total of 5 & 6	0.5M NaOH only
ME1	67	1.66	2.9	0.96	1.67	1.30	2.97	1.04
ME2	124	2.36	4.1	0.79	1.61	1.48	3.09	1.05
ME3	90	2.13	3.7	0.61	1.52	1.39	2.91	0.96
ME4	125	2.18	3.8	1.00	1.75	1.53	3.28	1.13
PG1	193	4.08	7.1	1.35	2.55	2.75	5.30	3.45
PG2	184	3.45	6.0	1.73	2.17	2.70	4.87	2.74
PG3	198	3.97	6.9	2.10	2.64	2.26	4.90	3.87
PG4	54	2.13	3.7	0.90	1.63	1.68	3.31	1.13
WM1	98	2.07	3.6	0.91	1.78	1.70	3.48	1.34
WM2	114	2.18	3.8	0.86	1.19	0.96	2.15	0.73
BALG	179	2.64	4.6	1.43	1.88	1.80	3.68	1.72
WB1	192	3.91	6.8	2.05	2.72	2.95	5.67	3.25
WB2	183	3.74	6.5	1.94	2.43	2.84	5.27	3.15
WB3	126	2.99	5.2	1.53	2.42	2.09	4.51	1.73
WL3	108	2.53	4.4	1.46	1.77	1.78	3.55	1.72
WL4	153	2.87	5.0	1.41	1.85	1.75	3.60	1.95
WL5	153	2.99	5.2	1.41	1.76	1.88	3.64	1.45
WL6	161	3.33	5.8	1.48	2.11	2.25	5.36	1.78
WL7	164	3.45	6.0	1.90	2.00	2.49	4.49	2.27
WL8	134	3.33	5.8	1.68	2.09	2.37	4.46	1.83
WL9	152	3.22	5.6	1.48	2.25	2.21	4.46	1.64
BAL1	120	3.56	6.2	1.69	1.64	2.16	3.80	1.97
BAL2	171	2.93	5.1	1.23	1.37	1.61	2.98	1.49
BAL3	135	2.07	3.6	0.99	1.08	1.29	2.37	1.20

Table A11 Results for Mean Weight Diameter and Determinations on Organic Matter and its Constituents for Soils of the Winton Series

SOIL	1	2	3	4	5	6	7	8
	Mean Weight Diameter M.W.D.	% Carbon	% Organic Matter	% Poly-saccharide	Optical Density of Humic Acid			
					0.1M $Na_2P_2O_7$	0.5M NaOH	Total of 5 & 6	0.5M NaOH only
W1	108	2.15	3.7	0.91	1.80	1.75	3.55	1.79
W2	85	2.35	4.1	1.02	2.02	1.57	3.59	1.54
W3	107	2.28	4.0	0.95	2.31	2.08	4.39	2.04
W4	190	4.06	7.1	1.91	2.55	3.65	6.20	3.84
HD5	119	2.28	4.0	1.01	2.87	2.52	5.39	2.86
HD6	87	2.10	3.7	0.94	1.87	2.15	4.02	2.11
HD7	77	2.39	4.2	0.82	1.88	2.30	4.18	1.80
BH8	141	2.26	3.9	0.93	1.85	2.33	4.18	2.39
BH9	65	2.15	3.7	0.83	2.03	2.58	4.61	2.35
DB10	165	3.29	5.7	1.38	1.53	1.78	3.31	1.82
DB11	96	1.73	3.0	0.84	1.52	1.58	3.10	1.46
DB12	121	1.88	3.3	0.86	2.00	2.17	4.17	2.00
DB13	76	1.86	3.2	0.80	1.53	1.84	3.17	1.38
CP14	85	1.74	3.0	0.84	1.92	2.10	4.02	2.05
CP15	93	1.74	3.0	0.94	2.04	2.02	4.06	1.87
TF16	126	3.31	5.8	1.47	2.42	2.81	5.23	3.48
PH17	100	3.11	5.4	1.10	2.11	2.40	4.51	2.61
FF18	156	4.01	7.0	1.29	2.17	3.42	5.59	3.15
HFR019	200	3.07	5.3	1.73	3.05	2.89	5.94	3.37
SR20	75	3.21	5.6	0.83	3.60	2.83	6.43	4.40
HD6S	39	0.64	1.1	0.31	2.08	0.78	2.86	0.80

Table A12 The Regression Equations for the Correlation Coefficients Presented in Table 8

Mean Weight Diameter and Organic Matter Content

where y = M W D and x = OM %

All Soils	y = 17x + 61
East of Scotland	y = 24x + 23
English	y = 15x + 67
Kilmarnock	y = 16x + 100
Humbie	y = 30x + 49
Stirling	y = 24x + 24
Winton	y = 20x + 24

Mean Weight Diameter and Polysaccharide Content

where y = M W D and x = Polysaccharide %

All Soils	y = 57x + 65
East of Scotland	y = 61x + 66
English	y = 48x + 67
Kilmarnock	y = 68x + 82
Humbie	y = 73x + 73
Stirling	y = 57x + 60
Winton	y = 104x + 3

Mean Weight Diameter and Pyrophosphate Extractable Humic Acid

where y = M W D and x = Optical density of H.A. soln

All Soils	y = 34x + 73
East of Scotland	y = 50x + 43
English	y = 34x + 79
Kilmarnock	y = 44x + 74
Humbie	y = 53x + 67
Stirling	y = 41x + 56
Winton	y = 18x + 71

Table A12 (continued)

Mean Weight Diameter and Sodium Hydroxide Extractable Humic Acid (after pyrophosphate extraction)

where y = M W D and x = Optical density of H.A. soln

All Soils	y = 33x + 73
East of Scotland	y = 47x + 34
English	y = 35x + 86
Kilmarnock	y = 25x + 105
Humbie	y = 70x + 32
Stirling	y = 58x + 24
Winton	y = 39x + 22

Mean Weight Diameter and the Sum of the Pyrophosphate Extractable and Sodium Hydroxide Extractable Humic Acid

where y = M W D and x = Optical density of H.A. soln

All Soils	y = 21x + 58
East of Scotland	y = 30x + 14
English	y = 22x + 68
Kilmarnock	y = 15x + 99
Humbie	y = 33x + 40
Stirling	y = 26x + 33
Winton	y = 20x + 22

Mean Weight Diameter and Sodium Hydroxide Extractable Humic Acid (separate soil sample)

where y = M W D and x = Optical density of H.A. soln

All Soils	y = 26x + 82
East of Scotland	y = 34x + 38
English	y = 30x + 88
Kilmarnock	y = 18x + 122
Humbie	y = 36x + 77
Stirling	y = 25x + 85
Winton	y = 24x + 54

BIBLIOGRAPHY

ACTON, C.J., RENNIE, D.A. and PAUL, E.A. (1963). The relationship of polysaccharide to soil aggregation. Can. J. Soil Sci. 43, 201-209.

AGRICULTURAL ADVISORY COUNCIL (1970). Modern farming and the soil M.A.F.F. H.M.S.O.

ALDERFER, R.B. (1950). Influence of seasonal and cultural conditions on aggregation of Hagerstown soil. Soil Sci. 69, 193-203.

ALEKSANDROVA, L.M. and NAD, M. (1958). The nature of organo-mineral colloids and methods for their study. Pochvovedenie 10, 21-27.

ALLISON, L.E. (1956). Soil and plant responses to V.A.M.A. and H.P.A.N. soil conditioners in the presence of high exchangeable sodium. Soil Sci. Soc. Amer. Proc. 20, 147-151.

ALLISON, L.E. and MOORE, D.C. (1956). Effect of V.A.M.A. and H.P.A.N. soil conditioners on aggregation, surface crusting and moisture retention in alkali soils. Soil Sci. Soc. Amer. Proc. 20, 143-146.

ARLIDGE, E.Z. and ANDERSON, G. (1962). The adsorption of inositol phosphates and glycerophosphates by soil clays, clay minerals and hydrated sesquioxides in acid media. J. Soil Sci. 13, 216-224.

ARMSTRONG, D.E. and CHESTERS, G. (1964). Properties of protein-bentonite complexes as influenced by equilibration conditions. Soil Sci. 98, 39-52.

ASPIRAS, R.B., ALLEN, O.N., CHESTERS, G. and HARRIS, R.F. (1971). The role of microorganisms in the stabilisation of soil aggregates. Soil Biol. Biochem. 3, 347-353.

BAB'YEVA, I.P. and MOAVAD, H. (1973). Soil yeasts of the genus Lipomyces as soil-conditioning agents. Soviet Soil Sci. 5, 430-432.

BACHE, B.W. (1970). Barium isotope method for measuring cation-exchange capacity of soils and clays. J. Sci. Fd. Agric. 21, 169-171.

BAILEY, G.W. and WHITE, J.L. (1970). Factors incluencing the adsorption, desorption and movement of pesticides in soil. Residue Rev. 32, 29-92.

BASCOMBE, C.L. (1964). Rapid method for the determination of cation-exchange capacity of calcareous and non-calcareous soils. J. Sci. Fd. Agric. 15, 821.

BEAN, A.G.M. and WELLS, D.A. (1953). Soil capping by water drops. Rep. no. 23. Nat. Inst. Agr. Engng., Silsoe, Beds.

BINGHAM, F.T., SIMS, J.R. and PAGE, A.L. (1965). Retention of acetate by montmorillonite. Soil Sci. Soc. Amer. Proc. 29, 670-672.

BISSADA, K., JOHNS, W.D. and CHENG, F.S. (1967). Cation-dipole interactions in clay-organic interactions. Clay Miner. 7, 155-166.

BLACK, C.A. (1965a). in Methods of soil analysis. (Black, C.A. ed. in chief). Agronomy No. 9, Part 2, Madison, Wis., p 1172.

BLACK, C.A. (1965b). in Methods of soil analysis. (Black, C.A. ed. in chief). Agronomy No. 9, Part 1, Madison, Wis., p 552.

BOND, R.D. and HARRIS, J.R. (1964). The influence of the microflora on the physical conditions of the soil. I. Effects associated with filamentous algae and fungi. Aust. J. Soil Res. 2, 111-122.

BOUYOUCOS, G.J. (1924). The influence of water on soil granulation. Soil Sci. 18, 103-108.

BRADFIELD, R. (1950). Soil structure. Proc. 4th Int. Cong. Soil Sci. 2, 9-19.

BRITISH STANDARDS INSTITUTION. (1975a). Methods of test for soils for civil engineering purposes. BS 1377, p 17.

BRITISH STANDARDS INSTITUTION. (1975b). Methods of test for soils for civil engineering purposes. BS 1377, p 19.

BRITISH STANDARDS INSTITUTION. (1975c). Methods of test for soils for civil engineering purposes. BS 1377, p 23.

BROWN, S.A. (1964). Lignin and tannin biosynthesis. In Biochemistry of phenolic compounds. Ed. J.B. Harbourne, 361-398.

BROWNING, G.M. (1937). Changes in the erodibility of soils brought about by the application of organic matter. Soil Sci. Soc. Amer. Proc. 2, 85-96.

BRYANT, J.C., BENDIXEN, T.W. and SLATER, C.S. (1948). Measurement of the water stability of soils. Soil Sci. 65, 341-345.

CAMERON, R.S., THORNTON, B.K., SWIFT, R.S. and POSNER, A.M. (1972). Molecular weight and shape of humic acid from sedimentation and diffusion measurements on fractionated extracts. J. Soil Sci. 23, 394-408.

CAMPBELL, D.J. (1974). Liquid limit determination of arable top-soils using a drop-cone penetrometer. Scot. Inst. Agric. Engng. Departmental note No. SSN/161.

CARR, C.E. and GREENLAND, D.J. (1972). Preliminary results of an empirical study of the movement of polymers through soils and their effect on the dispersion of clay from aggregates. Symposium on the fundamentals of soil conditioning, State Univ. of Ghent.

CHEPIL, W.S. (1954). Seasonal fluctuations in soil structure and erodibility of soil by wind. Soil Sci. Soc. Amer. Proc. 18, 13-16.

CHESHIRE, M.V. (1977). Origins and stability of soil polysaccharide. J. Soil Sci. 28, 1-10.

CHESHIRE, M.V. and ANDERSON, G. (1975). Soil polysaccharides and carbohydrate phosphates. Soil Sci. 119, 356-362.

CHESTERS, G., ATTOE, O.J. and ALLEN, O.N. (1957). Soil aggregation in relation to various soil constituents. Soil Sci. Soc. Amer. Proc. 21, 272-277.

CHILDS, E.C. (1940). The use of soil moisture characteristics in soil studies. Soil Sci. 50, 239-252.

CLAPP, C.E. and EMERSON, W.W. (1965). The effect of periodate oxidation on the strength of soil crumbs. I. Qualitative studies. II. Quantitative studies. Soil Sci. Soc. Amer. Proc. 29, 127-134.

CLEMENT, C.R. (1975). Ley fertility experiments at Hurley, in soil physical conditions and crop production. M.A.F.F. Technical Bulletin No. 29, 388-405.

CLEMENT, C.R. and WILLIAMS, T.E. (1958). An examination of the method of aggregate analysis by wet-sieving in relation to the influence of diverse leys on arable soils. J. Soil Sci. 9, 252-266.

CLOWES, F.A.L. and JUNIPER, B.E. (1968). Plant cells. Botanical Monographs. Vol. 8. Blackwell Scientific Publications Ltd., 203-214.

COOKE, G.W. (1967). The control of soil fertility. Crosby Lockwood & Son Ltd., London.

DE BOODT, M., DELEENHEER, L. and KIRKHAM, D. (1961). Soil aggregate stability indexes and crop growth. Soil Sci. 91, 138-146.

DE BOODT, M. (1972). Improvement of soil structure by chemical means, in optimising the soil physical environment towards greater crop yield. Ed. D. Hillel. Academic Press, New York.

DE LEENHEER, L. and DE BOODT, M. (1959). Mededel Landbouwhogeschool Opzoetugsstat. Staat. Ghent. 24, 257-266.

DESPHANDE, T.L., GREENLAND, D.J. and QUIRK, J.P. (1968). Changes in soil properties associated with the removal of iron and aluminium oxides. J. Soil Sci. 19, 108-122.

DETTMAN, M.G. and EMERSON, W.W. (1959). A modified permeability test for measuring the cohesion of soil crumbs. J. Soil Sci. 10, 215-226.

DI MARZIO, E. and McCRACKIN, F.L. (1965). One-dimensional model of polymer adsorption. J. Chem. Phys. 43, 539-547.

DOWDY, R.H. and MORTLAND, M.M. (1968). Alcohol-water interactions on montmorillonite surfaces. II. Ethylene glycol. Soil Sci. 105, 36-43.

DUBACH, P. and MEHTA, N.C. (1963). The chemistry of soil humic substances. Soils and Fert. 26, 293-300.

DUBOIS, M., GILLIES, K.A., HAMILTON, J.K., REBERS, P.A. and SMITH, F. (1956). Colourimetric method for determination of sugar and related substances. Analyt. Chem. 28, 350-356.

EAGLE, E.J. (1971). Ley fertility experiments. M.A.F.F. Tech. Bull. No. 20 125-144.

EAGLE, E.J. (1975). A.D.A.S. ley fertility experiments, in soil physical conditions and crop production. M.A.F.F. Technical Bulletin No. 29, 344-359.

ELLISON, W.D. (1952). Raindrop energy and soil erosion. Emp. J. Exp. Agr. 20, 81.

ELSON, J. (1941). A comparison of the effect of fertiliser and manure, organic matter, and carbon-nitrogen ratio on water-stable soil aggregates. Soil Sci. Soc. Amer. Proc. 6, 86-90.

EMERSON, W.W. (1954). The determination of the stability of soil crumbs. J. Soil Sci. 5, 233-250.

EMERSON, W.W. (1956). A comparison between the mode of action of organic matter and synthetic polymers in stabilising soil crumbs. J. Agric. Sci. 47, 350-353.

EMERSON, W.W. (1967). A classification of soil aggregates based on their coherence in water. Aust. J. Soil Res. 5, 47-57.

EMERSON, W.W. and GRUNDY, G.M.F. (1954). The effect of rate of wetting on water uptake and cohesion of soil crumbs. J. Agric. Sci. 44, 249-253.

EMERSON, W.W. and RAUPACH, M. (1964). The reaction of polyvinyl alcohol with montmorillonite. Aust. J. Soil Res. 2, 46-55.

ENSMINGER, L.E. and GIESKING, J.E. (1941). The adsorption of proteins by montmorillonite and its effect on base exchange capacity. Soil Sci. 51, 125-132.

ESTERMANN, E.F., PEARSON, G.H. and McLAREN, A.D. (1959). Digestion of clay-protein, lignin-protein and silica-protein complexes by enzymes and bacteria. Soil Sci. Soc. Amer. Proc. 23, 31-36.

EVANS, L.T. and RUSSELL, E.W. (1959). The adsorption of humic and fulvic acids by clays. J. Soil Sci. 10, 119-132.

FINCK, A. (1952). Ecological and pedological studies on the effects of earthworms on soil fertility. 2. Pflanzenernahr Düng. Bodenk. 58, 120-145.

FLAIG, W. and BEUTELSPACHER, H. (1951). Electron microscope investigations on natural and synthetic humic acids. 2. Pflanzenernahr Düng. Bodenk. 52, 1-21.

FLAIG, W. and BEUTELSPACHER, H. (1968). in. Isotopes and radiation in soil organic matter studies. International atomic energy agency. Vienna. pp 23-30.

FORD, G.W. and GREENLAND, D.J. (1968). The dynamics of partly humified organic matter in some arable soils. Trans. 9th Int. Cong. Soil Sci., Adelaide. 2, 403-410.

FORSYTH, W.G.C. (1950). Studies on the more soluble complexes of soil organic matter. 2. The composition of the soluble polysaccharide material. Biochem. J. 46, 141-146.

FRISCH, H.L. (1955). Polymer chain configuration near a boundary exerting forces. J. Phys. Chem. 59, 633-636.

FRISCH, H.L. and SIMHA, R. (1954). The adsorption of flexible marcromolecules 11. J. Phys. Chem. 58, 507-512.

GABRIELS, D.M., MOLDENHAUER, W.C. and KIRKHAM, D. (1973). Infiltration, hydraulic conductivity and resistance to water-drop impact of clod beds as affected by chemical treatment. Soil Sci. Soc. Amer. Proc. 37, 634-637.

GARWOOD, E.A., CLEMENT, C.R. and WILLIAMS, T.E. (1972). Leys and soil organic matter. III. J. Agric. Sci. 78, 333-341.

GEDROITS, K.K. (1955). Ibrannye Sochineniya 1, 409 (cited from KONONOVA, M.M. (1961). Soil organic matter (English translation) Pergamon Press, Oxford, 175-181.

GEOGHEGAN, M.J. (1950). Aggregate formation in soil. Influence of some microbial products and other substances on aggregation of soil particles. Trans. 4th Int. Cong. Soil Sci. 1, 198-201.

GIESKING, J.E. (1939). The mechanism of cation-exchange in the montmorillonite-beidellite-nontronite type of clay minerals. Soil Sci. 47, 1-11.

GILES, C.H., MacEWAN, T.H., NAKHWA, S.N. and SMITH, D. (1960). Studies in adsorption, Part II. A system of classification of solution adsorption isotherms. J. Chem. Soc. 3973-3993.

GILMOUR, C.M., ALLEN, O.N. and TRUOG, E. (1948). Soil aggregation as influenced by the growth of mould species, kind of soil and organic matter. Soil Sci. Soc. Amer. Proc. 13, 292-296.

GIOVANNINI, G. and SEQUI, P. (1976). Iron and aluminium as cementing substances of soil aggregates. J. Soil Sci. 27, 148-153.

GISH, R.E. and BROWNING, G.M. (1948). Factors affecting the stability of soil aggregates. Soil Sci. Soc. Amer. Proc. 13, 51-55

GREENLAND, D.J. (1963). Adsorption of polyvinyl alcohols by montmorillonite. J. Colloid Sci. 18, 647-664.

GREENLAND, D.J. (1965a). Interaction between clays and organic compounds in soils. Part 1. Mechanisms of interaction between clays and defined organic compounds. Soils and Fert. 28, 412-425.

GREENLAND, D.J. (1965b). Interaction between clays and organic compounds in soils. Part 11. Adsorption of soil organic compounds and its effect on soil properties. Soils and Fert. 28, 521-532.

GREENLAND, D.J. (1971). Interactions between humic and fulvic acids and clays. Soil Sci. 111, 34-41.

GREENLAND, D.J. (1972). Interaction between organic polymers and inorganic soil particles. Symposium on the fundamentals of soil conditioning, State Univ. of Ghent.

GREENLAND, D.J. and FORD, G.W. (1964). Separation of partially humified organic materials from soils by ultrsonic dispersion. Trans. 8th Int. Congr. Soil Sci., Bucharest. 3, 137-148.

GREENLAND, D.J., LABY, R.H. and QUIRK, J.P. (1962). Adsorption of glycine and its di-, tri- and tetra-peptides by montmorillonite and illite. Trans. Faraday Soc. 58, 829-841.

GREENLAND, D.J., LABY, R.H. and QUIRK, J.P. (1965). Adsorption of amino acids and peptides by montmorillonite and illite. Trans. Faraday Soc. 61, 2013-2035.

GREENLAND, D.J., LINDSTROM, G.R. and QUIRK, J.P. (1964). Role of polysaccharides in stabilisation of natural soil aggregates. Nature 191, 1283-1284.

GREENLAND, D.J., RIMMER, D. and PAYNE, D. (1975). Determination of the structural stability class of English and Welsh soils using a water coherence test. J. Soil Sci. 26, 294-303.

GRIFFITHS, E. and BURNS, R.G. (1972). Interaction between phenolic substances and microbial polysaccharides in soil aggregation. Plant and Soil 36, 599-612.

GRIFFITHS, E. and JONES, D. (1965). Microbiological aspects of soil structure. I. Relationships between organic amendments, microbial colonization and changes in aggregate stability. Plant and Soil 23, 17-33.

GRIM, R.E. (1968). Clay mineralogy. 2nd ed. McGraw-Hill, New York.

GUPTA, U.C., SOWDEN, F.J. and STOBBE, P.C. (1963). The characterisation of carbohydrate constituents from different soil profiles. Soil Sci. Soc. Amer. Proc. 27, 380-382.

HAIDER, K. and MARTIN, J.P. (1967). Synthesis and transformation of phenolic compounds by Epicoccum nigrum in relation to humic acid formation. Soil Sci. Soc. Amer. Proc. 31, 766-772.

HAIDER, K., MARTIN, J.P. and RIETZ, E. (1977). Decomposition in soil of ^{14}C-labelled coumaryl alcohols; Free and linked into dehydropolymer and plant lignins and model humic acids. Soil Sci. Soc. Amer. Proc. 41, 556-562.

HANK, R.J. and THORPE, F.C. (1957). Seedling emergence of wheat, grain, sorghum and soy beans as influenced by soil crust strength and moisture content. Soil Sci. Soc. Amer. Proc. 21, 357-359.

HARRIS, R.F., ALLEN, O.N., CHESTERS, G. and ATTOE, O.J. (1963). Evaluation of microbial activity in soil aggregate stabilisation and degradation by the use of artificial aggregates. Soil Sci. Soc. Amer. Proc. 27, 542-546.

HARRIS, R.F., CHESTERS, G. and ALLEN, O.N. (1966). Dynamics of soil aggregation. Adv. Agron. 18, 107-169.

HAWORTH, W.N. (1928). The constitution of sugars. Arnold, London.

HAYES, M.H.B. and SWIFT, R.S. (1978). The chemistry of soil organic colloids, in the chemistry of soil constituents. Marcel Dekker (in press), 179-320.

HENDRICK, R.M. and MOWRY, D.T. (1952). Effect of synthetic polyelectrolytes on aggregation, aeration, and water relationships of soil. Soil Sci. 73, 427-441.

HENDRICKS, S.B. (1941). Base-exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to Van der Waals forces. J. Phys. Chem. 45, 65-81.

HENIN, S. (1939). Influence of climatic factors on the structural stability of loam soils. Ann. Agron. 9, 301-311.

HENIN, S. (1944). Compt. Rend. Acad. Agr. France. 30, 373-375. Cited from Harris et al., (1966).

HENIN, S., MONNIER, G. and COMBEAU, A. (1958). Methods for the study of structural stability of soils. Ann. Agron. 9, 71-90.

HENIN, S., ROBICHET, O. and JONGERIUS, A. (1955). Principles concerned in assessing the stability of soil structure. Ann. Agron. Paris. 6, 537-557.

HIMES, F.L. and BARBER, S.A. (1957). Chelating ability of soil organic matter. Soil Sci. Soc. Amer. Proc. 21, 368-373.

HOPP, H. and HOPKINS, H.T. (1946). The effect of cropping systems on the winter population of earthworms. J. Soil Water Conserv. 1, 11-13.

HUBBELL, D.S. and CHAPMAN, J.E. (1946). The genesis of structure in two calcareous soils. Soil Sci. 62, 271-281.

INGRAM, Unpublished.

JOHNSTON, A.E. (1973). The effects of ley and arable cropping systems on the amounts of soil organic matter in the Rothamstead and Woburn by-arable experiments. Rothamstead Report for 1972, Part 2, 131-159.

KEEFER, R.F. and MORTENSON, J.F. (1963). Biosynthesis of soil polysaccharides. I. Glucose and alfalfa tissue substrates. Soil Sci. Soc. Amer. Proc. 27, 156-160.

KEMPER, W.D. and KOCH, E.J. (1966). Aggregate stability of soils from Western United States and Canada. U.S.D.A. Tech. Bull. No. 1355.

KOBO, K. and FUJISAWA, T. (1963). Studies on the clay-humus complex. 3. Adsorption of humic acid by clay. Soil Sci. and Plant Nutr. 9, 36-37.

KOLODNY, L. and NEAL, O.R. (1941). The use of micro-aggregation or dispersion measurements for following changes in soil structure. Soil Sci. Soc. Amer. Proc. 6, 91-95.

KONONOVA, M.M. (1961). Soil organic matter. Its nature, its role in soil formation and in soil fertility. Pergamon Press, Oxford.

KUNHELT, W. (1976). Soil biology. 2nd Ed. Faber and Faber, London.

LAW, J.P., Jr. and KUNZE, G.W. (1966). Reactions of surfactants with montmorillonite: adsorption mechanisms. Soil Sci. Soc. Amer. Proc. 30, 321-327.

LEMOS, P. and LUTZ, J.F. (1957). Soil crusting and some factors affecting it. Soil Sci. Soc. Amer. Proc. 21, 485-491.

LOW, A.J. (1975). Ley fertility experiments at Jealott's Hill in Soil Physical Conditions and Crop Production. M.A.F.F. Technical Bulletin No. 29, 324-343.

LOW, A.J., PIPER, F.J. and ROBERTS, P. (1963). Soil changes in ley arable experiments. J. Agr. Sci. 60, 229-238.

LUTZ, J.F. (1936). The relation of free iron in the soil to aggregation. Soil Sci. Soc. Amer. Proc. 1, 43-45.

LYNCH, D.L., WRIGHT, L.M., HEARNS, E.E. and COTNOIR, L.J. (1957). Some factors affecting the adsorption of cellulose compounds on clay minerals. Soil Sci. 84, 113-126.

MacEWAN, D.M.C. (1948). Complexes of clays with organic compounds. I. Complex formation between montmorillonite and halloysite and certain organic liquids. Trans. Faraday Soc. 44, 349-367.

MAHLER, H.R. and CORDES, E.H. (1966). Chemistry of carbohydrates in Biological chemistry. 2nd Ed. Harper and Row, New York. 465-487.

MARSHALL, T.J. (1956). A plummet balance for measuring the size distribution of soil particles. Aust. J. Appl. Sci. 7, 142-147.

MARSHALL, T.J. (1962). The nature, development and significance of soil structure. Trans. Commission IV and V Int. Soc. Soil Sci., 247-257.

MARTIN, A.E. (1960). Chemical studies of podzolic illuvial horizons. V. Flocculation of humus by ferric and ferrous iron and by nickel. J. Soil Sci. 11, 382-393.

MARTIN, A.E. and REEVE, R. (1960). Chemical studies of podzolic illuvial horizone. IV. The flocculation of humus by aluminium. J. Soil Sci. 11, 369-381.

MARTIN, J.P. (1946). Microorganisms and soil aggregation. Soil Sci. 61, 157-166.

MARTIN, J.P. (1971). Decomposition and binding action of polysaccharides in soil. Soil Biol. Biochem. 3, 33-41.

MARTIN, J.P., ERVIN, J.O. and RICHARDS, S.J. (1972). Decomposition and binding action in soil of some mannose-containing microbial polysaccharides and their Fd, Al, Zn and Cu complexes. Soil Sci. 113, 322-327.

MARTIN, J.P., ERVIN, J.O. and SHEPHERD, R.A. (1959). Decomposition and aggregating effectiveness of fungus cell material in soil. Soil Sci. Soc. Amer. Proc. 23, 217-220.

MARTIN, J.P., MARTIN, W.P., PAGE, J.B., RANEY, W.A. and DeMENT, J.D. (1955). Soil aggregation. Adv. Agron. 7, 1-37.

MARTIN, J.P. and WAKSMAN, S.A. (1941). Influence of microorganisms on soil aggregation and erosion: II. Soil Sci. 52, 381-394.

MARTIN, W.P., TAYLOR, C.S., ENGIBOUS, J.C. and BURNETT, E. (1952). Soil and crop responses from field applications of soil conditioners. Soil Sci. 73, 455-471.

MATSUDA, K. and SCHNITZER, M. (1972). The permanganate oxidation of humic acids extracted from acid soils. Soil Sci. 114, 185-193.

MAZURAK, A.P. (1950). Aggregation of clay separates from bentonite, kaolinite and a hydrous mica soil. Soil Sci. Soc. Amer. Proc. 15, 18-24.

McCALLA, T.M. (1944). Water drop method of determining stability of soil structure. Soil Sci. 58, 117-121.

McCALLA, T.M. (1946). Influence of some microbial groups on stabilising soil structure against falling water drops. Soil Sci. Soc. Amer. Proc. 11, 260-263.

McCALLA, T.M., HASKINS, F.A. and FROLIK, E.F. (1957). Influence of various factors on aggregation of Peorian Loess by microorganisms. Soil Sci. 84, 155-161.

McHENRY, J.R. and NEWELL, L.C. (1947). Influence of some perennial grasses on the organic matter content and structure of an Eastern Nebraska fine-textured soil. J. Amer. Soc. Agron. 39, 981-994.

McHENRY, J.R. and RUSSELL, M.B. (1944). Elementary mechanics of aggregation of puddled materials. Soil Sci. Soc. Amer. Proc. 8, 71-78.

McINTYRE, D.S. (1958). Soil splash and the formation of surface crusts by raindrop impact. Soil Sci. 85, 261-266.

McNEAL, B.L. (1964). Effect of exchangeable cations on glycol retention by clay minerals. Soil Sci. 97, 96-102.

MEHTA, N.C., STREULI, H., MÜLLER, M. and DEUEL, H. (1960). Role of polysaccharides in soil aggregation. J. Sci. Food Agric. 11, 40-47.

MEHTA, N.C., DUBACH, P. and DEUEL, H. (1963). Examination of the molecular weight distribution of humic acids by gel filtration through sephadex. Z. PflErnähr Düng. 102, 128-137.

METSON, A.J. (1956). Methods of chemical analysis for soil survey samples. Wellington, New Zealand.

MEYER, L. (1935). Preparation and use of humus-clay mixtures. Z. PflErnähr Düng. 19, 211-224.

MONTOMURA, K. and MATUURA, R. (1969). Conformation of adsorbed polymeric chains. J. Chem. Phys. 50, 1281-1287.

MORTENSON, J.L. (1962). Adsorption of hydrolysed polyacrylonitrile on kaolinite. Clays and Clay Minerals. Proc. 9th Nat. Conf. 530-545.

MORTLAND, M.M. (1970). Clay-organic complexes and interactions. Adv. Agron. 22, 75-117.

MORTLAND, M.M. and RAMAN, K.V. (1968). Surface acidity of smectites in relation to hydration, exchangeable cation, and structure. Clays Clay Miner. 16, 393-398.

MYINT, C.C. (1975). Organic matter changes in soils from ley fertility experiments. Ph.D. Thesis. Aberdeen University.

NORTH, P.F. (1976). Towards an absolute measurement of soil structural stability using ultrasound. J. Soil Sci. 27, 451-459.

OADES, J.M. (1967). Carbohydrates in some Australian soils. Aust. J. Soil Res. 5, 103-115.

OADES, J.M. (1974). Synthesis of polysaccharides in soil by micro-organisms. Trans. 10th Int. Cong. Soil Sci. (Moscow). 3, 93-99.

OLMSTEAD, L.B. (1946). The effect of long-time cropping systems and tillage practices upon soil aggregation at Hays, Kansas. Soil Sci. Soc. Amer. Proc. 11, 89-92.

PANABOKKE, C.R. and QUIRK, J.P. (1957). Effect of initial water content on stability of soil aggregates in water. Soil Sci. 83, 185-189.

PARFITT, R.L. and GREENLAND, D.J. (1970a). The adsorption of poly (ethylene glycols) on clay minerals. Clay Minerals. 8, 305-316.

PARFITT, R.L. and GREENLAND, D.J. (1970b). Adsorption of polysaccharides by montmorillonite. Soil Sci. Soc. Amer. Proc. 34, 862-866.

PERCIVAL, E.G.V. (1955). Structural carbohydrate chemistry. Garnet Miller, London.

PERROT, K.W., LANGDON, A.G. and WILSON, A.T. (1974). Sorption of phosphate by aluminium and iron (III) - hydroxy species on mica surfaces. Geoderma. 12, 223-231.

PETERSON, J.B. (1947). Calcium linkage, a mechanism in soil granulation. Soil Sci. Soc. Amer. Proc. 12, 29-34.

PRINGLE, J. and COUTTS, J.R.H. (1956). The effect of grasses on aggregation in light soils. J. Brit. Grassland Soc. 11, 185-189.

PUGH, A.L., VOMOUL, J.A. and NIELSEN, T.R. (1960). Modification of some physical characteristics of soils with V.A.M.A., ferric sulphate and triphenylbulfonuum chloride. Agron. J. 52, 399-402.

QUIRK, J.P. (1950). The measurement of stability of micro-aggregates in water. Aust. J. Agric. Res. 1, 276-284.

RANEY, W.A. (1953). Soil aggregate stabilisers. Soil Sci. Soc. Amer. Proc. 17, 76-77.

RENNIE, D.A., TRUOG, E. and ALLEN, O.N. (1954). Soil aggregation as influenced by microbial gums, level of fertility and kind of crop. Soil Sci. Soc. Amer. Proc. 18, 399-403.

RETZER, J.L. and RUSSELL, M.B. (1941). Differences in the aggregation of a prairie and a Gray-Brown Podzolic soil. Soil Sci. 52, 47-58.

REUHRWEIN, R.A. and WARD, D.W. (1952). Mechanism of clay aggregation by polyelectrodytes. Soil Sci. 73, 485-492.

ROBINSON, D.O. and PAGE, J.B. (1950). Soil aggregate stability. Soil Sci. Soc. Amer. Proc. 15, 25-29.

ROE, R.J. (1965). Conformation of an isolated polymer molecule at an interface. II. Dependence on molecular weight. J. Chem. Phys. 43, 1591-1598.

ROST, C.O. and ROWLES, C.A. (1941). A study of the factors affecting the stability of soil aggregates. Soil Sci. Soc. Amer. Proc. 5, 421-433.

ROTHAMSTEAD EXPERIMENTAL STATION. (1970). Details of the classical and long-term experiments up to 1967. Harpenden.

RUSSELL, E. (1923). The microorganisms of the soil. Longmans, Green and Co., London.

RUSSELL, E.J. (1950). Soil conditions and plant growth. 8th ed, Longmans and Green, New York. pp 397-420.

RUSSELL, E.J. and VOEKLER, J.A. (1936). Fifty years of field experiments at the Woburn Experimental Station. Rothamstead Monographs on Agricultural Science. Longmans, Green and Co., London. pp 392.

RUSSELL, E.W. (1938). Imperial Bureau of Soil Science, Harpenden, England. Tech. Commun. 37, 1-40.

RUSSELL, E.W. (1961). Soil conditions and plant growth. 9th ed, Longmans and Green, New York. pp 430-446

RUSSELL, J.D. (1965). Infra-red study of the reactions of ammonia with montmorillonite and saponite. Trans. Faraday Soc. 61, 2284-2293.

RUSSELL, M.B. and FENG, C.L. (1947). Characterisation of the stability of soil aggregates. Soil Sci. 63, 299-304.

RYCROFT, D.W. and THORBURN, A.A. (1974). Water stability tests on clay soils in relation to mole draining. Soil Sci. 117, 306-310.

SALE, P.J.M. (1964). The growth of established lettuce plants as affected by soil capping. J. Hort. Sci. 89, 162-172.

SCHAHABI, S. and SCHWERTMANN, U. (1970). Effect of synthetic iron oxides on aggregation of two loess horizons. Z. PflErnähr.

SCHARPENSEEL, H.W. (1966). Formation and type of bonding of clay-humic acid complexes. Z. PflErnähr Düng. Bodenk. 114, 175-203.

SCHNITZER, M. and SKINNER, S.I.M. (1964). Organo - metallic interactions in soils. 3. Properties of iron- and aluminium -organic matter complexes, prepared in the laboratory and extracted from soil. Soil Sci. 98, 197-203.

SCHNITZER, M. and KODAMA, H. (1966). Montmorillonite : effect of pH on its adsorption of a soil humic compound. Science 173, 70-71.

SHERWOOD, P.T. and RYLEY, M.D. (1970). An investigation of a cone-penetrometer method for the determination of the liquid limit. Geotechnique 20, 203-208.

SIDERI, D.I. (1936). On the formation of structure in soil : II. Synthesis of aggregates; on the bonds uniting clay with sand and clay with humus. Soil Sci. 42, 461-481.

SIDERI, D.I. (1938). On the formation of structure in soil. IV. The structure of mixed clay-sand and clay-humus formations. Soil Sci. 46, 129-137.

SILBERBERG, A. (1962a). Adsorption of flexible macromolecules. I. The isolated macromolecule at a plane interface. J. Phys. Chem. 66, 1872-1883.

SILBERBERG, A. (1962b). Adsorption of flexible macromolecules. II. The shape of the adsorbed molecule; the adsorption isothem; surface tension. J. Phys. Chem. 66, 1884-1907.

SILBERBERG, A. (1967). Adsorption of flexible macromolecules. III. Generalized treatment of the isolated macromolecule. J. Chem. Phys. 46, 1105-1114.

SILBERBERG, A. (1968). Adsorption of flexible macromolecules. IV. Effect of solvent - solute interactions, solute concentrations, and molecular weight. J. Chem. Phys. 48, 2835-2851.

SIMHA, R., FRISCH, H.L. and EIRICH, F.R. (1953). Adsorption of flexible macromolecules. J. Phys. Chem. 57, 584-589.

SIMPSON, K. and HAYES, S.F. (1958). The effect of soil conditioners on plant growth and soil structure. J. Sci. Food Agric. 9, 163-170.

SLATER, C.S. (1953). Effect of sample drying on the determination of the water stability of soils. Soil Sci. Soc. Amer. Proc. 17, 75-76.

SLATER, C.S. and HOPP, H. (1949). The action of frost on the water stability of soils. J. Agr. Res. 78, 341-346.

SMITH, R.M. and BROWNING, D.R. (1946). Influence of evacuation upon laboratory percolation rates and wetting of undisturbed soil samples. Soil Sci. 62, 243-253.

SPIERS, R.B. (1976). Personal communication.

STALLINGS, J.H. (1953). Continuous organic matter supply - the key to soil aggregation and biological activity. J. Soil Water Conserv. 8, 178-184.

STEFANSON, R.C. (1971). Effect of periodate and pyrophosphate on the seasonal changes in aggregate stabilisation. Aust. J. Soil Res. 9, 33-41.

SWABY, R.J. (1949). The relationship between microorganisms and soil aggregation. J. Microbiol. 3, 236-254.

SWIFT, R.S. and POSNER, A.M. (1972). Nitrogen, phosphorus and sulphur contents of humic acids fractionated with respect to molecular weight. J. Soil Sci. 23, 50-57.

SWINCER, G.D., OADES, J.M. and GREENLAND, D.J. (1969). Extraction, characterisation and significance of soil polysaccharides. Adv. Agron. 21, 195-235.

TAYLOR, G.S. and BALDRIDGE, P.E. (1954). The effect of sodium carboxymethylcellulose on some physical properties of Ohio soils. Soil Sci. Soc. Amer. Proc. 18, 382-385.

THENG, B.K.G. (1974). The chemistry of clay-organic reactions. Hilger, London. 365pp.

TINSLEY, J. (1950). The determination of organic carbon in soils by dichromate mixtures. Trans. 4th Int. Cong. Soil Sci. 1, 161-164.

TIULIN, A.F. (1928). Question of soil structure. II. Aggregate analysis as a method for determining soil structure. Perm. Agric. Exp. Sta. Div. Agric. Chem. Rept. 2, 77.

TIULIN, A.F. (1954). Questions of soil structure in forests. Pochvovedenie. 1, 30-44.

TIULIN, A.F. and KOSOVKINA, A.V. (1950). The different quality of water stable aggregates in relation to the group composition of secondary particles smaller than 0.01 mm. Pochvovedenie. 3, 142-150.

TOOGOOD, J.A. and LYNCH, D.L. (1959). Effect of cropping systems and fertilisers on mean weight diameter of aggregates of Breton plot soils. Can. J. Soil Sci. 39, 151-156.

TOWNER, G.D. (1973). An examination of the fall-cone method for the determination of some strength properties of moulded agricultural soils. J. Soil Sci. 24, 470-479.

VAN BAVEL, C.H.M. (1949). Mean weight diameter of soil aggregates as a statistical index of aggregation. Soil Sci. Soc. Amer. Proc. 14, 20-23.

WAKSMAN, S.A. and STEVENS, K.R. (1930). A critical study of the methods for determining the nature and abundance of soil organic matter. Soil Sci. 30, 97-116.

WARD, H.S. Jnr. (1949). Reactions of adapted legumes and grasses on the structural condition of eroded Lindley - Weller soils in South-Eastern Iowa. Ecol. Monographs. 19, 145-171, cited from Soils and Fert. (1950) 13, 1408.

WEAKLEY, H.E. (1960). The effect of H.P.A.N. soil conditioner on run off, erosion and soil aggregation. J. Soil Wat. Conserv. 15, 169-171.

WEBER, J.B., PERRY, P.W. and UPCHURCH, R.P. (1965). The influence of temperature and time on the adsorption of paraquat, diquat, 2, 4 - D and prometone by clays, charcoal and an anion - exchange resin. Soil Sci. Soc. Amer. Proc. 29, 678-688.

WEISMULLER, W. (1965). Investigations on the fractionation of soil organic matter. Albrecht - Thaer - Arch. 9, 419-436.

WHITEHEAD, D.C., BUCHAN, H. and HARTLEY, R.D. (1975). Components of soil organic matter under grass and arable cropping. Soil Biol. Biochem. 7, 65-71.

WHISTLER, R.L. and KIRBY, K.W. (1956). Composition and behaviour of soil polysaccharides. J. Amer. Chem. Soc. 78, 1755-1759.

WILLIAMS, B.G. (1965). The influence of poly (vinyl alcohol) on the physical properties of soil aggregates. Ph.D. Thesis, Univ. of Adelaide. cited from CARR, C.E. and GREENLAND, D.J. (1972).

WILLIAMS, B.G., GREENLAND, D.J., LINDSTROM, G.R. and QUIRK, J.P. (1966). Techniques for the determination of the stability of soil aggregates. Soil Sci. 101, 157-163.

WILLIAMS, B.G., GREENLAND, D.J., and QUIRK, J.P. (1968). Water stability of natural clay aggregates containing polyvinyl alcohol. Aust. J. Soil Res. 6, 59-66.

WILLIAMS, R.J.B. (1970). Relationships between the composition of soils and physical measurements made on them. Rothamstead Experimental Station. Report for 1970, Part 2, 5-35.

WILLIAMS, R.J.B. and COOKE, G.W. (1961). Some effects of farmyard manure and of grass residues on soil structure. Soil Sci. 92, 30-39.

WILLIS, W.O. (1955). Freezing and thawing and wetting and drying in soils treated with organic chemicals. Soil Sci. Soc. Amer. Proc. 19, 263-267.

YARIV, S., RUSSELL, J.D. and FARMER, V.C. (1966). Infra-red study of the adsorption of benzoic acid and nitrobenzene on montmorillonite. Israel J. Chem. 4, 201-213.

YODER, R.E. (1936). A direct method of aggregate analysis of soils and a study of the physical nature of soil erosion losses. Amer. Soc. Agron. J. 28, 337-351.